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Water Quality
and Treatment

Water Quality and Treatment

A HANDBOOK OF PUBLIC WATER SUPPLIES

Prepared by
The American Water Works Association, Inc.

Third Edition

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WATER QUALITY AND TREATMENT

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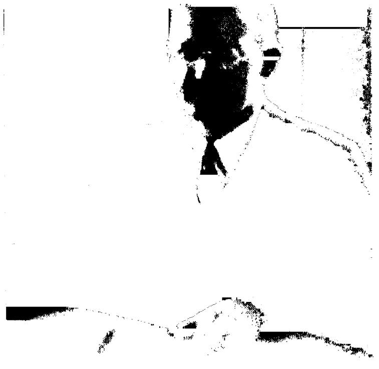

Dedication

We who have worked on the preparation of this book over the years since the second edition appeared in 1950, want to dedicate this third edition to the late John R. Baylis, (1885–1963) a diligent research worker who contributed prodigiously to the art of water purification. He greatly influenced his immediate associates toward improved plant design and operation, as well as a multitude of friends and admirers acquired as a result of his extensive work on corrosion control, water quality standards, and water purification.

Born in Eastabuchie, Mississippi, John Baylis grew up in the pine woods of his native state. He was trained as a civil engineer at Mississippi State College, worked for several years in railroad design and construction, then gravitated as designer to the Jackson, Mississippi, Filtration Plant, soon becoming its operating head. This was one of the earliest plants to be provided with a baffled flocculating basin. He moved to Baltimore in 1917 to operate the Montebello filters where, with Abel Wolman's help, he developed one of the earliest working electrometric pH units and applied it in the control of flocculation and corrosion.

When, in 1926, Chicago decided to establish a 1.0-mgd experimental filtration plant, Baylis was selected to head it, remaining there in research and guiding design of the South District Filtration Plant until 1944, when the plant was placed in service. He then served as Engineer of Water Purification for the City of Chicago until his death on October 31, 1963.

An indefatigable worker, Mr. Baylis was usually at his office or laboratory from 8 A.M. until after 5 P.M. and, through many of the years of his career, continued his work in the evening. Thus, he was able to publish hundreds of original contributions in various trade and professional journals. His research was characterized by the exactness of his observations, which he recorded in minute detail leading to important, fundamental conclusions based on what he had observed. His associates remember him as a kindly, dedicated man.

AWWA recognized Mr. Baylis' contributions by awarding him the Fuller, Diven, and John M. Goodell Awards and Honorary membership. NEWWA twice gave him the Dexter Brackett Medal, and ASCE accorded him the James Laurie Prize.

Chapter 7 in this book, "Filtration," was drafted by Mr. Baylis at the age of 77, and edited by two of his close associates. It reflects John R. Baylis' careful observations and deductions about one of the important unit processes in water treatment.

Preface

Like the first and second editions, this, the third edition, of "Water Quality and Treatment" was developed as a public-service activity of the American Water Works Association. The purpose of the book is to present authoritative information on water quality and on water-treatment principles and practice. It is the sincere hope of the authors, editors, and the Association that the material included will be of interest and benefit to water utility managers, treatment-plant operators, engineers, chemists, bacteriologists, biologists; in fact, all who are closely associated with the vital daily task of supplying large volumes of quality water to the public. If the book is of assistance, in some small measure, to these men in the achievement of excellence in their daily service to the public, the many hours of work that went into its preparation will have been worthwhile. In addition, it is hoped that the book will prove valuable as a reference source to teachers and students interested in water quality and its enhancement through treatment.

The decision to prepare a third edition was made in June 1961 by the officers of the Water Purification Division (now the Water Quality Division) with the advice and consent of the officers and directors of the Association.

A six-member Revision Committee was formed and revision work was begun in July 1961.

The material presented in this edition is the result of the voluntary efforts of many individuals. Each chapter represents the work of one or more authors who are identified with the various chapters. Their task was not an easy one, for much has been learned about the art and science of water treatment in the nearly twenty years that have passed since the publication of the second edition. These are the men who made the book possible and they, of course, have the sincere thanks of the Association and the Revision Committee. In addition, they deserve the thanks of all who may find the book useful.

Technical editing of the authors' chapter drafts was done by Martin E. Flentje and Raymond J. Faust.[1] David B. Preston, AWWA Assistant Executive Director coordinated publication and editorial activities at Association headquarters. These individuals also made a substantial contribution to the third edition of "Water Quality and Treatment" and their valuable assistance is acknowledged with thanks.

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[1] Mr. Faust served as Executive Secretary of the Association from 1959 until retirement in 1967.

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Water Quality and Treatment

1

Water Quality

By DR. J. A. BORCHARDT
and DR. GRAHAM WALTON

The term "water quality" is a widely used expression which has an extremely broad spectrum of meanings. Each individual has vested interests in water for his particular use, which may involve commercial and industrial uses or recreational pursuits. Since the desirable characteristics of a water vary with its intended use, there is frequently unsatisfactory communication among the users of water where quality is concerned. Thus in discussing a public supply, a housewife may declare the water to be of good quality, while a brewmaster considers the quality to be poor.

All other water uses must be subordinated to man's need for a healthful fluid for his consumption. Water for drinking and food preparation must be free from organisms capable of causing disease and from minerals and organic substances producing adverse physiological effects. To encourage man to drink this health-promoting liquid, the water must be aesthetically acceptable. For example, it should be free from apparent turbidity, color, and odor and from any objectionable taste. Drinking water also should have a reasonable temperature. Such water is termed "potable," meaning that it may be consumed in any desired amount without concern for adverse effects on health.

Potable water is so readily available in the United States that few people consider its abundance as a modern miracle. One can travel from coast to coast freely consuming water from any public water-supply tap without feeling constrained to ask whether the water is "safe." This general acceptance of the "safety" of public water supplies is a dramatic tribute to the achievements of the waterworks industry, the state and local departments of health, and the U.S. Public Health Service.

There are many parts of the world, however, where potable water is still relatively unavailable. A recent publication of the World Health Organization states that every 24 hours 13,000 children under 1 year of age will die primarily because of waterborne diseases.[1]

The widespread availability of "safe" water should not be interpreted as meaning that all of the nearly 21,000 community waterworks in this country have no deficiencies in the operation and control of their water systems. Such a conclusion would be far from the truth. To meet the consumers' demands for greater volumes and better-quality water, water utilities in a rapidly growing country must expand at least as fast as the population.

In addition, many water-treatment plants have experienced difficulty in producing aesthetically satisfactory water from sources polluted with industrial, municipal, or agricultural wastes.

Water quality is dynamic, and its changing parameters require the water technologist to be in constant touch with many segments of the scientific world. The chemist, the bacteriologist, the biologist, and the toxicologist are making advances in the assessment and quantization of water quality parameters. However, other segments of science are generating new products and new water contaminants at an ever-increasing rate. Man himself is multiplying and his range is increasing. The products of population growth and industrial development are reflected in a deteriorating water quality in previously unaffected areas of the country.

In the past, the water supply industry in many regions has been quite fortunate to have been able to obtain adequate quantities of raw water of good quality, even though it sometimes had to be transmitted across long distances. In the future, there will be many instances where a water utility will have to accept water of lower quality and treat it as necessary to produce water meeting the consumers' needs. As a result water quality acquires increased significance, and man must define more exactly those parameters which for the most part have been quite subjective during the development of our society.

HISTORICAL NEEDS FOR WATER QUALITY CRITERIA

Historically, fertile river valleys with abundant water seem to have been the centers for the beginnings of civilization. The greatest use of water was for irrigation and agricultural pursuits, while only a small amount was consumed by the people. The use of water for drinking and cooking was limited to that amount that people could carry from the well or the stream in their jugs, pots, and other vessels.

It seems a curious fact that, while water is an absolute necessity for life, little was recorded by ancient historians regarding the quality of drinking water. Certain brief references were made to boiling, filtering, sedimentation, and treatment of water with salts. Since man knew relatively little about disease, it must be concluded that any treatment had as its objective the improvement of the appearance or taste of the water. No definite standards of quality other than general clarity or palatability were recorded by ancient civilizations.

In 1771, the first edition of the *Encyclopaedia Britannica* defined a filter as "a strainer, commonly made of bilbous or filtering paper in the form of a funnel in order to separate the gross particles from water and render it limpid."[2] This definition stresses the filtration of water and establishes filtration as an effective means of producing limpidity. In the older literature, the state of being limpid was reserved for a stream into which one could peer and see the bottom perfectly. Today, a water man would describe such a stream as being without noticeable turbidity or color. Thus it seems that the general practice of making water clear was well recognized, but the degree of clarity was not measurable.

Hippocrates, the father of medicine (460 to 354 B.C.), stated that "water contributes much to health," and asserted that rainwater should be boiled and strained, for otherwise it would have a bad smell and cause hoarseness. Herodotus, one of the first Greek historians, reports that Cyrus the Great, king of Persia, when going to war took boiled water in silver flagons loaded on four-wheel carts drawn by mules. Reports are that this water was boiled to make it keep, which again reflects concern for the aesthetic properties of the water.[3] Historical records indicate that standards of water quality, except for infrequent reference to aesthetics, were notably absent up to and including much of the nineteenth century. Even today most people will first look at the water in a glass to see if it is crystal clear and sparkling. Then they will taste it to see if it is palatable. If the water is agreeable to them in these basic respects, they assume that it is of high quality.

Warm distilled water is of high quality, but distasteful. Thus one certainly cannot accurately judge the quality of drinking water by sensory perceptions. Many examples might be cited to illustrate how man's sense of taste and smell failed him with serious consequences. One example is the story of the Broad Street Well cholera epidemic as summarized by Rosenau:[4]

> . . . cholera was prevalent in London in 1854, but prevailed with epidemic intensity in the district about Broad Street.
>
> No less than 700 deaths occurred in St. James Parish in the 17 weeks that the cholera raged. John Snow made a very detailed study of the situation

> and associated the epidemic with the Broad Street Well and a leaky sewer which passed adjacent to this well, bringing infection from the original cholera case in the house at No. 40 Broad Street. While the area close by the well had many hundreds of cases, there were sporadic outbreaks of cholera in other parts of the City of London, which were also investigated by Snow. Quoting from his report, "The deaths of Mrs. E and her niece, who drank water from Broad Street at the West End, Hampstead, deserve especially to be noticed. I was informed by Mrs. E's son that his mother had not been in the neighborhood of Broad Street for many months. A cart went from Broad Street to West End every day, and it was the custom to take out a large bottle of the water from the pump in Broad Street, as she *preferred* it."

In another place, Snow's inquiry showed that most of the victims had preferred or had access to water from the Broad Street Well. Apparently, its contamination with some sewage did not impair its flavor, since so many people preferred this well water. It might even be assumed that the people using water from this well were accustomed to the taste of the slightly polluted water and thus took extra efforts to procure this supply; or it might have been that other available water tasted worse.

It does not take much pollution to cause disease. Rosenau's text mentions that "the typhoid epidemics at Butler, Plymouth, New Haven, Nanticoke, and Reading, involving 39,029 cases with 361 deaths, were caused in each epidemic by the careless treatment of the discharges of one individual patient."[5]

Man's reliance on taste and smell has not been an infallible means of judging the acceptability of water; more stringent quality criteria have been a necessary historical development.

Referring again to the writings of Hippocrates, it would appear that his interest in water centered on the selection of the most health-giving source of supply rather than on purifying the waters that were bad. Apparently, ancient people deduced by observation that certain waters promoted good health, while others produced infection. And, while they knew nothing about the causes of disease, they appeared, at least in some instances, to have been astute enough to recognize the health-giving properties of pure and wholesome water. Unfortunately, such information had to be acquired through the illness and death of many people.

This ability to observe and correlate facts reached such heights that in 1852 a law was passed in London that all water thenceforth should be filtered.[6] This was about 50 years after the first municipal filtration works was built in Paisley, Scotland,[7] and approximately 10 years before Pasteur and others demonstrated the germ theory of disease.[8]

By 1900 there were probably no more than 10 slow-sand water filtration plants in the United States.[9] The record suggests that a century of observations on death by waterborne disease was necessary to firmly clarify the facts as demonstrated by generalized public observations. There is no question that lack of communication greatly retarded scientific progress, and that the time required for association of cause and effect was a product of many sociological factors.

In retrospect it seems obvious that progress toward improving man's health and welfare could result only from better control over his environment. The provision of better-quality water was one logical step in this direction.

BACTERIOLOGICAL EXAMINATION OF WATER

The bacteriological examination of water is a rather recent development. Normally, fecal contamination is indicated by the presence of a group of organisms designated by the term "coliform." In the past, such organisms have been referred to in literature as *B. coli, Bacterium coli, Bacillus colon, Escherichia coli*, or *E. coli*. The term "coliform group" is the present connotation, and it implies that these organisms are a bacterial group of unknown dimensions rather than a single species.✓

In 1884 Escherich isolated from the stools of a cholera patient organisms which he originally thought to be the cause of that disease. Further investigations, however, showed that similar organisms also were present in the intestinal tracts of healthy individuals. From this beginning, the existence of the coliform organisms has come to be recognized as an inherent characteristic of the feces of man. Perhaps one-third to one-fifth of the weight of the average individual's feces are active viable coliform organisms. In terms of population equivalent, this amounts to 200×10^9 coliform cells per capita per day. The presence of these organisms in water may be interpreted to mean that such water has been contaminated with fecal matter.

While the work of Escherich suggested the value of *E. coli* as indicators of fecal contamination, it remained for Theobald Smith,[10] about a decade later, to establish procedures for inoculating fermentation tubes with measured volumes of the water being tested. The New York State Board of Health first applied this procedure in 1892 in their study of pollution of the Mohawk and Hudson Rivers.[11]

The 1914 U.S. Treasury Department standards specified that an acceptable drinking water must not show presence of *B. coli* in more than one of the five 10-ml portions of the sample tested. The terminology *B. coli* was retained in the 1925 standards, but the examination of a series of samples rather than appraisals of individual samples was stressed. This realization of the statistical nature of a set of observations was a significant advance. By 1942, the term had changed from *B. coli* to "coliform group." The membrane filter (MF) procedure was first included as an alternate to the multiple-tube procedure in the 1962 standards.

Standard Methods for the Examination of Water and Wastewater[12] defines the coliform group as including "all of the aerobic and facultative anaerobic, Gram-negative, non-spore-forming rod-shaped bacteria which ferment lactose with gas formation within 48 hours at 35 °C." The coliform group includes both fecal and nonfecal bacteria. They are the predominant organisms that are found in the intestinal tract of man and other animals, both warm-blooded and cold-blooded.[13] Certain nonfecal soil bacteria, such as *Aerobacter aerogenes*, are also included in this group. Although bacteriological procedures have been developed which measure only the fecal coliform, health-oriented personnel agree that the examination of drinking water should be based on all bacteria of the coliform group. Presence in drinking water of significant numbers of any members of the coliform group indicates either deficiencies in treatment of the water or inadequate protection of the source of an untreated water. Laboratory procedures for both the MPN dilution and the MF methods for coliform bacterial examination of water are given in *Standard Methods*.[12]

The MF procedure has the advantage of securing the results in less time. It also requires less work and less incubator space. Geldreich et al.,[14] however, note that both skillful and careful laboratory work is required to secure satisfactory results.

> The membrane filter procedure will yield accurate and reliable results when it is carried out by experienced people using accepted materials and procedures. This method, however, does require more skill and personal judgment than are necessary for the MPN test. There will be occasional water samples, with their great variety of pollutants, for which the MF procedure should not and cannot be used. In such instances, the multiple tube technic is the method of choice. However, the MF technic can be and is being used on a routine basis by many water laboratories. It must be understood that more attention should be paid to proper MF methodology. With proper care as to size of sample, medium preparation, time and temperature for incubation, and colony sheen discernment, the MF is an excellent bacteriological tool capable of yielding a more precise and rapid answer than is available from the multiple tube MPN test.

Importance of Bacteriological Control

The incidence of a disease-producing organism in raw water is related to the endemic level of the particular disease within the tributary population. Cholera has not been prevalent in the United States since the 1880s.[15] There have been only three epidemics of amoebic dysentery in the United States in modern times. Available evidence indicates that each of these epidemics resulted from pollution introduced through cross connections between potable and contaminated water systems.[16] Typhoid continued as a serious problem into the 1900s with high prevalence and high death rate.[17] Typhoid fever has now been practically eliminated as a waterborne disease through appropriate bacteriological control of finished water quality (see Fig. 1) and immunology.

A health benefit frequently overlooked when the quality of water is improved is sometimes known as "Hazen's theorem." In 1904 Allen Hazen presented a quantitative expression for death rates from other diseases as related to those for typhoid fever.[18] As it was expressed at the time, when one death from typhoid fever is avoided by the use of a better water, two or three deaths from other causes are also avoided. This proposition also was noted by others and is sometimes referred to as the "Mills-Reincke phenomenon," named for Hiram F. Mills, a civil engineer of Lawrence, Massachusetts, and Dr. J. J. Reincke of Hamburg, Germany. These gentlemen reported somewhat similar information at virtually the same time. Two factors that may be presumed to have contributed to this phenomenon are: first, when the human system is freed from having to resist typhoid infection, it has greater resistance to other diseases; and second, better treatment results in water relatively free from organisms causing diseases other than typhoid. At Hamburg, Germany, for example, for each decrease in death from typhoid fever after installation of filtration, there were 15.8 fewer deaths from other causes. At Lawrence, Massachusetts, this

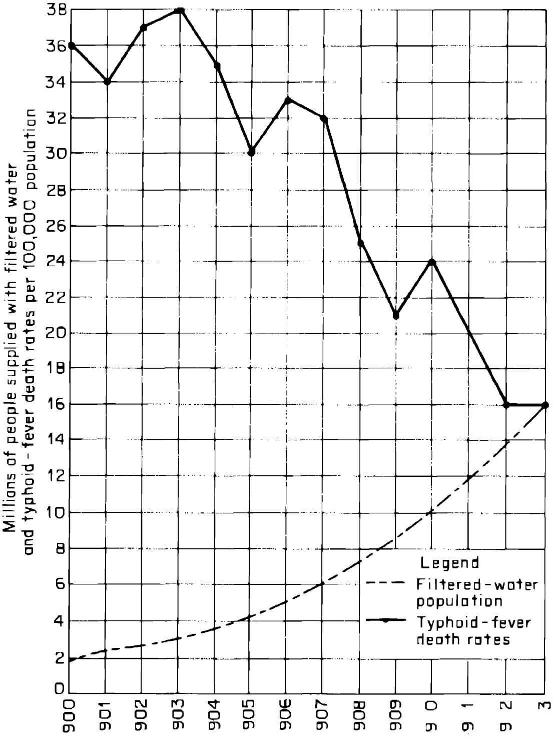

Fig. 1 Growth of water filtration and decrease in typhoid-fever death rate in the registration cities of the United States. *Note:* Since 1952 the death rate from typhoid fever in the United States has been less than 0.1/100,000.

ratio was 1:4.4. At Lowell, Massachusetts, it was 1:6.0. At Albany, New York, it was 1:1.5.[19] Statistics showing the decrease in the death rate from typhoid fever accompanying the advent of water purification practice usually fail to emphasize this additional benefit.

As previously stated, the coliform organisms, because of the large numbers present in fecal matter, offer a far more satisfactory approach to the detection of the presence of fecal contamination than would a search for the pathogenic organisms. Since the incidence of pathogens is related to the presence of infected persons in the community, there may be long periods of time when fecal contamination is present, but specific pathogens would be absent. Thus, a search for a specific pathogenic organism might be fruitless. Moreover, throughout the time required to make the necessary examinations, people would continue to consume the water. This delay in determining the hazardous nature of a water could easily result in a waterborne-disease outbreak. Furthermore, test procedures would have to be definitive for all of the organisms causing the various waterborne diseases. Such a procedure is not presently available, nor is it likely to be developed in the near future. Although the waterworks profession relies on the coliform examination to determine whether water is free from disease-producing microorganisms, this test for water safety does have its limitations. What is the response of other biological organisms to the various treatment processes? Can it be assumed that the treatment reduces all pathogenic organisms to the same extent that it reduces coliform bacteria?

Accumulated evidence indicates that the bacteria causing typhoid, paratyphoid, cholera, and bacillary dysentery respond to treatment in the same manner as coliform bacteria.[20] Some viruses, however, appear to persist in water for longer times than coliform.[21] Viruses may penetrate through rapid-sand filters more readily than coliform bacteria.[22] Certain viruses are known to be more resistant than coliform to destruction by chlorine disinfection.[23,24] From these observations, one can only conclude that it is possible for certain pathogenic organisms to survive treatment that apparently removes or destroys all coliform bacteria.

Despite this possibility the record of waterborne-disease outbreaks attributable to properly treated public water supplies indicates that the coliform bacterial examination has served as a satisfactory measure of the microbiological safety of water. This may be attributed to several factors: man's natural immunities, the low incidence of waterborne disease in the population, and the fact that many raw waters, particularly the more polluted ones, are treated by processes providing good clarification and heavy chlorination. With good clarification and exposure to substantial levels of free chlorine residual over extended periods of time, there is an excellent chance of removing or destroying any virus that may be present in the raw water.

Considerable research is being done in the area of water bacteriology. Fecal streptococcus is being studied, cultured, and compared to fecal coliform.[25] Virus culturing techniques are being studied and improved.[26] Gastroenteritis is being studied to better define the causative agent as well as its control.[27] Through such efforts, microbiological pollution control will keep pace with future developments.

THE ROLE OF CHEMICAL ANALYSIS IN WATER QUALITY

During the latter part of the nineteenth century, before bacteriological examination became accepted, the safety of water was evaluated by chemical methods. The relative concentrations of ammonia nitrogen, nitrates, nitrites, and albuminoid nitrogen were used to indicate the presence and amount of recent pollution. Water was considered to be safe when the predominant amounts of nitrogenous matter were in the oxidized forms. The use of such chemical tests to evaluate the bacteriological safety of water failed to prevent outbreaks of waterborne disease.[28] With the acceptance of bacteriological procedures, together with increased knowledge of the role which microorganisms have in causing disease, bacteriological examinations replaced chemical analyses as the means of determining whether water was free from disease-producing organisms.

The time required to complete a bacteriological examination of water prevents direct utilization of this test in routine water plant operation. This deficiency is overcome at plants that disinfect the water with chlorine by use of residual chlorine analysis. By correlating the amount and type of residual chlorine in the finished water with the results of its bacteriological examination, it is possible for each plant to determine the chlorine residual required to ensure production of water that is free, or essentially free, from coliform bacteria. The residual-chlorine test is undoubtedly the most important of all chemical analyses used to control the quality of drinking water.

Those concerned with the establishment of the first United States Standards for Drinking Water were unable to reach an agreement on the health-related aspects of physical or chemical parameters. The Public Health Service Standards for Drinking Water, 1914, specified bacteriological but not chemical or physical requirements. Limiting concentrations for copper, lead, and zinc were included in the 1925 standards, and the 1946 standards contained seven additional chemical substances. The list of chemical substances whose presence in excessive amounts are undesirable or even cause for rejection of water for drinking purposes was expanded in the 1962 standards.

Although it is generally accepted that present drinking water standards establish satisfactory control of microbiological quality, the possible health hazard associated with chemical pollutants is a matter of increasing concern. To quote from a recent paper by two outstanding authorities:[20]

> Today the new challenge facing the water supply profession is the control and removal of the hazardous nonliving contaminants—the chemicals and isotopes which are being produced in a bewildering array of new compounds. It is to be expected that some of these chemicals, as well as the wastes from their production, enter public water supplies. Unfortunately, very little is known about the extent of the pollution of the nation's water supplies by these new chemicals which include many commercial poisons.

Obviously, because of the fears implied in this quotation, it must be expected that the chemical characteristics in any future revision of the standards will necessarily become more complex.

It seems important at this point to outline certain critical potable water philosophies to clarify the bases on which chemical standards might be established. In reporting on the 1914 standards, the USPHS advisory commission decided that their problem was to recommend "not standards of purity, but limits of impurities." The public water supply must be free from injurious effects on the human body and likewise be acceptable for man's many uses. Potable water must be free from objectionable taste, odor, color, turbidity, and other physical defects. It must not deteriorate in the distribution system or in storage; and it must not aggressively attack the distribution system or the consumer's plumbing.

Space does not permit thorough discussion of the standards and delineation of the pertinent philosophy involved in their adoption. (Refer to the appendix at the end of this chapter for further information on this subject.) Nevertheless, discussion of the considerations involved in establishing a single standard may be of value.

Lead was first included in the 1925 standards. The tolerance level was 0.1 mg/l. This value remained unchanged in the 1942 and 1946 standards, but it was reduced to 0.05 mg/l in the 1962 standards. Toxicologically, lead is a cumulative poison, though man may excrete as much as 0.3 mg/day. The amount of lead deposited on fruit and vegetables sprayed with lead compounds used for insect control can be significant, but the residual lead on the marketed foods has been reduced to a minimum by washing or other processing procedures required by health authorities. Although the use of lead compounds for insect control is decreasing, the amount of lead from other sources, such as industrial fumes, cigarette smoking, and tetraethyl lead from gasoline, is certainly increasing. One can only conclude that the lead intake through the lungs into the human body is on the increase. Since it is economically possible for most waterworks to limit the lead content of the water delivered to the consumer, the 1962 standards reduced the level from 0.1 to 0.05 mg/l. Thus, there are many aspects of the environment which must be considered before a standard is set. The specified limiting value may have little apparent connection with a known toxicological quantity, except to those who were intimately associated with its selection.

It seems logical to expect that future standards will become more complex as water reuse is practiced. To some extent this will depend upon the development of analytical procedures and instrumentation which will provide relatively easy means for measurement of trace amounts of the more exotic constituents in water. Fear has been expressed that future standards may become too intricate and involve too many parameters for efficient administration.

An alternative to development of such involved standards lies in the feasibility of purifying water so thoroughly, by demineralizing and other processes, that it will be desirable to reconstitute it. The reconstituted water would be pure H_2O plus those few constituents desired to produce optimum characteristics within the distribution system and the human body. As reconstitution of water involves much the same philosophy as that involved in fluoridation, it might be attacked in accordance with a reasoning—that of whether it is right to apply medication to drinking water. Philosophically it is one of the major missions of all waterworks personnel to treat water for the purpose of preventing disease.

Fluorine and chlorine are closely related elements that are applied to water to protect the health of the consuming population. Chlorine is used to disinfect water and thus prevent waterborne outbreaks of typhoid and other enteric diseases. Fluorine is added to water to reduce the occurrence of dental caries among those consuming the water. This also is a preventive measure. When health professionals decide that fluoridation of a public water supply is the best means for providing this health protection, the waterworks industry should accept the responsibility of adding the necessary element. Actually, most public water supplies contain fluoride, and a few contain too much. When there is too much fluoride in the water, its reduction to prevent mottling of tooth enamel is accepted as being good public health practice.

Fluoridation of water was first practiced at Grand Rapids, Michigan. It was started January 25, 1945, as an experiment to determine whether fluorides artificially added to water containing little or no natural fluoride would reduce dental caries in the local population to the level found among populations consuming water supplies naturally containing near-optimum fluoride concentrations. The results of the Grand Rapids and many similar studies have fully demonstrated that proper fluoridation of the water supply results in substantial reduction of tooth decay among the consuming population. Artificial fluoridation of water has proven to be an excellent and inexpensive health benefit. It is a major public health program that is practiced extensively in the United States.

Since its inception, there has been much opposition, both on ethical and legal grounds, to artificial fluoridation of public water supplies. Pro-fluoridation decisions by state courts and finally by the U.S. Supreme Court have settled the legal question. The ethical issue has subsided. Recently the legislatures of two states have granted their state departments of health authority to order fluoridation of public water supplies. The public is gradually understanding and accepting the benefits of fluoridated water.

Chemical analysis involves important factors other than just toxicological considerations. For example, should a public water supply taste or look unpalatable, the consumer may prefer to seek another source and in so doing may be trading a safe but unappealing water for a hazardous but more palatable alternate. Thus, it is inappropriate for a water utility to produce a safe but unattractive water. The waterworks industry acknowledges its responsibility for providing aesthetically satisfactory water of uniform quality. At times fulfillment of this responsibility is difficult: the public may not be fully informed as to the cost and practicability of eliminating unsavory water characteristics and consequently they may be reluctant to pay for it.

Whenever a sudden change in the characteristics of a surface water supply affects the aesthetic quality of the treated water, it may indicate the presence of a new pollutant. In such cases an effort must be made immediately to identify the polluting substance and to provide corrective treatment to safeguard the supply and to prevent deterioration of the aesthetic quality of the water delivered to the consumers.

Procedures for making rapid changes in plant operation to cope with emergencies are mandatory for good, responsible plant operation. In spite of the extra treatment costs for correcting periodic aesthetic problems, the effort must be made even if no direct health implications have been demonstrated. While chemical analyses are important in determining the finished water's compliance with standards, they are essential for control of treatment-plant operation.

WATER QUALITY RELATIVE TO TIME AND PLACE

In 1900 the best-quality drinking water that could be produced from a river source was defined by the experiments carried on at the Lawrence Experiment Station in Cambridge, Massachusetts. Those studies showed that slow-sand filtration treatment of local river water could reduce the *Escherichia coli* to 66 per 100 ml. By 1914, the first U.S. Treasury Standards established a quality requirement for water of approximately 2 *Escherichia coli* organisms per 100 ml (the introduction of chlorination in 1907 having made this remarkable improvement possible). In 1925 the U.S. Public Health Service established bacteriological standards which limited the average *B. coli* count in drinking water to approximately 1 per 100 ml. During this period of approximately 25 years the quality of drinking water as measured by its bacterial content improved tremendously. Such change had to proceed hand in hand with the engineer's accomplishments in developing processes that could produce this improved quality of water. It must be recognized, however, that as long as it remains impossible to study such organisms as the infectious hepatitis virus, our knowledge of microbiology of water is not complete.

WATER QUALITY RELATIVE TO USE

From the user's point of view the term "water quality" is used to define those chemical, physical, biological, or radiological characteristics by which he evaluates the acceptability of the water. The quality of a raw water may or may not be acceptable to the user. If it is unsatisfactory, a treatment plant can be designed to produce acceptable-quality water. The term "quality" must therefore be considered relative to the proposed use of the water. One might speak of a water as being of poor quality, medium quality, or excellent quality when it comes to satisfying an individual.

Those involved in water quality needs are thinking more and more in terms of its multiple use. The field of water resources is in a state of change as attempts are made to define the various qualities of water necessary for each of its many uses. If one considers water from an abstract point of view and superimposes the problem of inadequate amounts of high-quality water, it seems quite logical to place all uses in order of their importance. Water for human consumption would come first. This would be followed by all other uses including carriage of waste. Unfortunately, the same water that is used for human consumption is also used for the lowest-level purpose, that of flushing wastes to a point of disposal. There are major problems in providing separate water supplies for drinking and waste disposal. It is not feasible to construct a wall down the center of our streams to provide separate channels, one for clean, unimpaired fresh water and the other for wastewater. This places other users of water, particularly one's downstream neighbors, in the position of having to contend with water which has been used to some extent by others.

Reuse of water, then, has become a necessity in many cases. This may be repugnant to many who think of used water only as reflecting an inherently distasteful quality as well as possibly having infectious characteristics.

On the other hand, water that falls from the sky is merely water which has been evaporated, possibly from a polluted source elsewhere on the face of the earth. If we can take polluted water and, by evaporation, produce water as pure as rain, no consumer should object. Even so, if it were a man-made and man-operated process with sewage as the raw ingredient, this particular system would probably be objectionable to many. The Chanute[30] and Santee[31] experiences indicate that the public attitude toward utilization of water can be changed. The public's concept of reuse and their emotional and hysterical reactions can be replaced by common sense and regard for scientific facts. Obviously, as our population grows, the need to reuse water will increase. Already there are cities using water from rivers whose contents have been used many times by upstream consumers. This practice is countenanced because the waste involved is discharged to a natural stream. Somehow, if nature intercedes, the resulting mixture becomes more acceptable. The city of Philadelphia, for example, utilizes water that has been used by many villages and towns before it reaches the city of Philadelphia. It has been estimated that during some months of the year this water can be used and reused a total of 17 times before it reaches Philadelphia, where it is once again treated before being pumped to that city's distribution system.

The Neosho River that flows through the state of Kansas has a similar problem which has been outlined very ably in the *Journal of the American Water Works Association.*[30] It is estimated that the various cities along this river use the total volume of flow from four to seven times during its passage through the state. During one drought period, the city of Chanute, Kansas, was on the verge of having little or no water. This problem was solved by constructing a temporary earthen dam across the river to back the sewage plant effluent through a rather long lagoon up to the water plant intake. Thereafter, the treated sewage was recirculated through the lagoon up to the water plant intake. The same water was treated and used an estimated six or seven times by the inhabitants of Chanute before the drought ended some 7 months later. Although this water was bacteriologically safe and available for drinking, it was not an aesthetically satisfactory water.

Judgment Factors in Water Quality

The treatment of water to produce a safe and satisfactory product for public use has been called an "art" rather than a "science." Many of the decisions involved in treating water are based on inexact rather than exact scientific knowledge. Through the years, those concerned with water supply have established guidelines, but these, too, have usually involved judgment in interpreting the applicable scientific knowledge.

The microbiological safety of drinking water is determined by its being examined for coliform bacteria, an indicator rather than a pathogenic organism. The generally accepted standard requires that a minimum number of samples, based on the population served, shall be examined each month, and that the average coliform density for all samples examined during each month shall not exceed approximately 1 per 100 ml. Two assumptions have been made: first, that the coliform content of the water actually examined is truly representative of that of the water delivered to the consumer; and second, that water containing an average of not more than cne coliform bacteria per 100 ml is free from disease-producing bacteria. The individuals responsible for developing the standards recognized that these assumptions resulted in a small but finite health hazard. Results of investigations of waterborne epidemics have shown that drinking water meeting these bacterial standards has rarely been incriminated in the transmission of waterborne disease. The records indicate that good judgment was used in establishing these standards.

Certain chemical analyses of the water are made routinely at most water plants, but the frequency of making them may vary greatly. For example, at one plant treating a water subject to large, sudden variations in chlorine demand, the plant superintendent found it desirable to install a residual-chlorine recorder equipped with an alarm to alert the operator if the chlorine fell below a preset value. At other plants, treating raw waters of uniform quality, chlorine residuals are determined at intervals of 2 or more hours. Good judgment plus information gained with experience in treating the water dictate the desired frequency of the residual-chlorine determinations. At most plants, analyses for toxic substances in the treated water are made at infrequent intervals, usually not more than once or twice a year. In most cases this practice would be acceptable to the health agencies, but if a water is known to contain or is suspected of containing potentially toxic amounts of a substance, good judgment requires collection of sufficient information to determine need for possible corrective action.

Periodically, a water utility should evaluate its capabilities for continuing to supply adequate volumes of safe and satisfactory water. This evaluation, commonly called a "sanitary survey," includes the appraisal of the source and treatment of the water, its storage and distribution, and its bacteriological, physical, and chemical quality. Consideration is given to the capabilities of the waterworks in meeting past and future demands and, if needed, to the preparation of plans for supplemental water supplies, additional treatment facilities, and additions to the distribution system. Of particular importance, as indicated by the records of waterborne-disease outbreaks, is an appraisal of sanitary defects in the distribution system. Obviously such an evaluation requires both knowledge and judgment on the part of the individual making the sanitary survey.

Those who deal with the USPHS Drinking Water Standards on a relatively casual basis in many cases have the impression that the standards are set strictly on a physiological or health basis. To some extent the legal profession tends to assume this point of view also. Several selected quotations from a recent article are presented in order to give the background of logic as applied by a lawyer to the points in question.[32]

> It may be helpful to evaluate briefly the potential areas of civil liability of water purveyors, and the ways in which compliance with the USPHS Drinking Water Standards, including the proposed new revision, can be used to minimize such liability. One of the legal bases for liability for supplying unsafe drinking water is negligence of the supplier.
>
> A supplier of drinking water may be held liable for negligence if he falls below the standard of good practice in supplying the water and the consumer is thereby injured. . . . Another approach to liability that has been gaining widespread acceptance in recent years in cases involving suppliers of products such as machinery, food, and drugs, is the doctrine of implied warranty. According to this doctrine, when a purchaser of goods relies on a seller's skill and judgment in making his purchase, and has made known to the seller the purpose for which the goods are required, the sale gives rise to an implied warranty or promise on the part of the seller that the goods are reasonably fit for the purpose for which they are purchased. If the purchaser is injured because of a lack of such fitness, the seller is liable, regardless of whether or not he was negligent, so long as the vendor has had an opportunity to examine the article sold. . . . At the present time, however, compliance with the standards would seem to provide the best available line of defense against liability based on implied warranty.
>
> The present widespread respect for the USPHS Drinking Water Standards would seem to dictate caution in recommending drastic modification, unless it is clearly necessary for the further protection of the public health. . . . But the very respect with which the present standards are now regarded would suggest that only such changes be made as can be clearly justified, so that respect may be retained and strengthened.

This point of view reflects the legal judgment that involves injury as one aspect in the establishment of a standard. Other disciplines, too, might desire from one or more points of view that the aspect of injury be associated with the upper margin of tolerance established by the standards. In reality, no stated value in the present standards has such an exact basis. Some values in the standards involve aesthetics, others economical treatment, and with others perhaps even the elements of convenience may enter into the final decision.

Development of the Public Health Service Drinking Water Standards

On October 21, 1914, pursuant to the recommendation of the Surgeon General of the Public Health Service, the Treasury Department adopted the first standards[33] for drinking water supplied to the public by any common carrier engaged in interstate commerce. These standards specified the maximum permissible limits of bacteriological impurity, which may be summarized as follows:

1. The bacterial plate count on standard agar incubated for 24 hr at 37°C was not to exceed 100/cc.

2. Not more than one of the five 10-cc portions of each sample examined was to show presence of *B. coli.*

3. The recommended procedures were those in *Standard Methods of Water Analysis* (APHA, 1912).

These standards were drafted by a commission of 15 appointed members. Among the members of this commission were Charles Gilman Hyde, Milton J. Rosenau, William T. Sedgwick, George C. Whipple, and C. E. A. Winslow, names well known to those who have studied early developments in water treatment.

Though not a part of the standards, the accompanying first progress report is very interesting as it provides insight into the commission's deliberations on other problems. There appears to have been considerable discussion on whether the standards should also state that the water shall "be free from injurious effects upon the human body and free from offensiveness to the sense of sight, taste, or smell"; whether the quality of water required should be obtainable by the common carriers without prohibitive expense; and whether it would be necessary to require more than a "few and simple examinations to determine the quality of drinking water."

Although this commission noted the value of a field or sanitary survey, their report clearly shows that the samples of water to be examined were to be taken from the carrier. It is also evident that the recommended and accepted standards were limited to the bacteriological quality only because the commission had been unable to agree on specific physical and chemical requirements.

The advisory committee responsible for preparing the 1925 standards[34] defined a "safe water" as one from which "the risk of infection is very small compared to the ordinary hazards of life" and utilized the concept of availability (the quality of the better municipal supplies) for guidance in establishing the standards.

The principal changes introduced in the 1925 standards may be summarized as follows:

1. The water supply was now to be obtained from a source free from pollution, adequately protected by natural agencies against the effects of pollution, or adequately protected by artificial treatment.

2. The bacteriological requirement was more restrictive. Not more than 10 per cent of all 10-ml portions examined were permitted to show presence of the *B. coli* group organisms. At the same time, this requirement did permit three or more of the five 10-ml portions examined to show presence of *B. coli* in not more than 5 per cent of the samples examined. The examining period and number of samples required to determine compliance with the standard were not specified.

3. The water was to be clear, colorless, odorless, and pleasant to the taste and was not to contain an excessive amount of soluble mineral substances

or of any of the chemicals used in the treatment processes. Although analyses were not required, the finding of lead, copper, or zinc in excess of specified concentrations constituted grounds for rejecting a supply.

The 1942 standards[35] were prepared by a "special Advisory Committee composed of representatives of various federal organizations and scientific associations and . . . several members at large." A smaller subcommittee of Public Health Service officers was designated to prepare tentative suggestions for the consideration of the advisory committee.

The principal changes from the 1925 standards were:

1. A distinct separation of the text into two parts, one containing the Standards, and the other the Manual of Water Works Practice, which represented the judgment of the technical subcommittee composed of Public Health Service officers. The latter was "intended to serve as a guide to the reporting agency" and was "not to be considered as indicating additional requirements to be met for certification of the water supply."
2. In the bacteriological section the examination of either five 10-ml or five 100-ml portions was made optional; a minimum number of samples, depending on the population served, was to be examined each month; and the laboratories and procedures used in making these examinations were subject to inspection at any time by a designated representative of the certifying authority.
3. Maximum permissible concentrations were established for lead, fluoride, arsenic, and selenium. Salts of barium, hexavalent chromium, heavy metal glucosides, or other substances having deleterious physiological effects were not allowed in the water supply systems. In general, semiannual analyses for these substances were considered to be satisfactory tests of concentration.
4. Maximum concentrations which should not be exceeded where more suitable water supplies were available were given for copper, iron plus manganese, magnesium, zinc, chloride, sulfate, phenolic compounds, total solids, and alkalinity.
5. In recognition of the problems resulting from faulty plumbing practices and faulty water plant and distribution system operational practices, there was included the statement that "The water supply system in all its parts shall be free from sanitary defects and health hazards and shall be maintained at all times in a proper sanitary condition."

The 1946 standards[36] were essentially the same as the 1942 standards except for:

1. The restatement of certain requirements to make the standards "generally acceptable and applicable to all water supplies in the United States."
2. The omission from the standards and separate publication of the *Manual of Recommended Water Sanitation Practice.* This was done

because all too frequently the manual had been interpreted as being part of the standards.

3. A maximum permissible concentration was added for hexavalent chromium, and the wording which excluded presence of salts of barium, hexavalent chromium, heavy metal glucosides, and other substances having deleterious physiological effects in the water system was changed to prohibit their use in water-treatment processes.

The objective of the advisory committee for the 1962 standards[37] was to recommend minimum requirements for domestic water supplies to protect the health and promote the well-being of individuals and the community. Assistance to this committee was provided by a technical subcommittee of Public Health Service officers and a toxicological task force whose duties consisted of collecting information and preparing suggestions for consideration by the committee.

As the complete text of the 1962 standards is given in the appendix to this chapter (page 37), only a few major changes will be noted. These are:

1. The requirement that the water-supply system be properly operated under the supervision of qualified personnel
2. The inclusion of the membrane filter (MF) procedure as an alternate method for bacteriological examination of water
3. The addition of permissible or recommended maximum limiting concentrations for alkyl benzene sulfonate, barium, cadmium, carbon chloroform extract, cyanide, nitrate, and silver
4. The consideration of water consumed by an individual as determined by climate in establishing the limited levels of fluorides in fluoride-treated water
5. The addition of a new section on radioactivity
6. The addition of an appendix explaining the rationale used by the committee in establishing the limiting concentrations of various chemicals, etc.

Somewhat greater detail on the development of the Public Health Service Drinking Water Standards is shown in Table 1-1, which compares the bacteriological, physical, and chemical requirements and recommendations of each of the various standards.

In accordance with the recommendation made by the advisory committee responsible for the development of the 1962 standards, the Public Health Service established an Advisory Committee on Use of the Public Health Serivce Drinking Water Standards. This committee has continued to appraise the quality requirements for drinking water and has recommended certain changes and additions for inclusion in the Public Health Drinking Water Standards. These changes and additions, as given in the Manual for Evaluating Public Drinking Water Supplies,[38] are:

1. Chemicals present should not exceed the following concentrations:

Substance	*Concentration, mg/l*
Boron (B)	1.0
Fluoride (F)	
50.0–58.3 °F[a]	1.8
58.4–70.6 °F[a]	1.5
70.7–90.5 °F[a]	1.2
Nitrogen (N), nitrate plus nitrite	10.0
Uranyl ion (UO_2)	5.0

Substances not specifically included in the standards should not be present in concentrations which may have deleterious physiological effects or which may be excessively corrosive to the water supply system.

2. Pesticides present should not exceed the following concentrations:

Pesticide	*Concentration, mg/l*[b]
Aldrin	0.017
Chlordane	0.003
DDT	0.042
Dieldrin	0.017
Endrin	0.001
Heptachlor	0.018
Heptachlor epoxide	0.018
Lindane	0.056
Methoxychlor	0.035
Total organophosphorous and carbamate compounds in forms of parathion equivalent cholinesterase inhibitions	0.1
Toxaphene	0.005
2,4-D[c] 2,4,5 T 2,4,5 TP	0.1

[a] Annual average of maximum daily air temperatures.

[b] For long-time exposure.

[c] Exposure to 0.1 mg/l of 2,4-D should be limited to only 2 to 3 days, no more than once or twice a year.

COMPARISON OF VARIOUS DRINKING WATER STANDARDS AND GOALS

This section compares some of the more pertinent requirements and recommendations of the World Health Organization's European Standards for Drinking Water, 1961,[39] the World Health Organization's International Standards for Drinking Water, 1963,[40] the Public Health Service Drinking Water Standards, 1962, and the American Water Works Association's Quality Goals for Potable Water, 1968.[41]

TABLE 1-1 Development of the U.S. Public Health Service Drinking Water Standards

Criterion	1914	1925	1942	1946	1962
A. Bacteriological Constituents					
Plate count	Total bacterial count on agar plate not to exceed 100 per ml				
Coliform bacteria (*B. coli* prior to 1942) *a*. Dilution technique (five 10-ml portions)	Not more than one of the five portions examined from each sample shall show presence of *B. coli* (*B. coli* MPN $\leq$ 2.2 per 100 ml)	1. Not more than 10% of all portions examined shall show presence of *B. coli* (*B. coli* $\leq$ 1.0 per 100 ml) 2. Not more than 5% of all samples examined shall show presence of *B. coli* in three or more of the five portions examined	1. Not more than 10% of all portions examined each month shall show presence of coliform bacteria (coliform MPN $\leq$ 1.0 per 100 ml) 2. No two consecutive samples taken from the same location, and not more than one (or 5%) of all samples examined each month, shall show presence of coliform bacteria in three or more of the five portions	Same as 1942	Same as 1942
b. Dilution technique (five 100-ml portions)			1. Not more than 60% of all portions examined each month shall show presence of coliform bacteria (coliform MPN $\leq$ 0.9 per 100 ml)	Same as 1942	Same as 1942

TABLE 1-1 Development of the U.S. Public Health Service Drinking Water Standards *(Continued)*

Criterion	1914	1925	1942	1946	1962
A. Bacteriological Constituents					
			2. No two consecutive samples taken from the same location, and not more than one (or 20%) of all samples examined each month, shall show presence of coliform bacteria in all five portions examined		
c. MF technique (using 50, 100, 200, or 500 ml)					1. The arithmetic mean coliform count for all samples examined each month shall not exceed one per 100 ml 2. The coliform count shall not exceed three per 50 ml, four per 100 ml, seven per 200 ml, or thirteen per 500 ml in two consecutive samples taken from the same location, nor in more than one (or 5%) of all samples examined each month

TABLE 1-1 Development of the U.S. Public Health Service Drinking Water Standards *(Continued)*

Criterion	1914	1925	1942	1946	1962
A. Bacteriological Constituents					
Frequency of sampling	Not specified	Not specified	Specified by certifying authority	Regulated jointly by reporting agency and certifying authority	Same as 1946
Minimum number of samples to be examined in specified period	Not specified	Not specified	A minimum number, dependent on population served, shall be examined each month	Same as 1942	Same as 1942 except for an increased number per population served
Laboratory procedures	1912 *Standard Methods*	1923 *Standard Methods*	1936 *Standard Methods*	Current edition of *Standard Methods*	Current edition of *Standard Methods*
Inspection of laboratories	Not specified	Not specified	Subject to inspection by certifying authority	Subject to inspection by certifying and reporting agencies	Same as 1946

TABLE 1-1 Development of the U.S. Public Health Service Drinking Water Standards *(Continued)*

B. Physical Constituents

Criterion	Recommended limit (Concentrations which should not be exceeded when more suitable water supplies can be made available)					Tolerance limit (Concentrations in excess of those listed shall constitute grounds for rejection of the supply)				
	1914	1925	1942	1946	1962	1914	1925	1942	1946	1962
Color, units	....	20, preferably 10	....	20	15	....	....	20	20[a]	
Odor, threshold number	....	Generally acceptable	....	Not objectionable	3, inoffensive	....	....	Not objectionable		
Residue:										
Filtrable, mg/l	....	....	....	....	500					
Total, mg/l	....	....	500	500	....	....	....	1,000	1,000	
Taste	....	Generally acceptable	....	Not objectionable	Inoffensive	....	....	Not objectionable		
Turbidity, units	....	....	....	10	5	....	....	10	10[a]	
Frequency of sampling	....	Not specified	Not specified	Not specified	At least once each week					
Minimum number of samples to be examined in specified period	....	Not specified	Not specified	Not specified	Not specified					

C. Chemical Constituents

Substance	Recommended limit, mg/l (Concentrations which should not be exceeded when more suitable water supplies are available)					Tolerance limit, mg/l (Concentrations in excess of those listed shall constitute grounds for rejection of the supply)				
	1914	1925	1942	1946	1962	1914	1925	1942	1946	1962
Alkyl benzene sulfonate (ABS)	....	.....	......	....	0.5					
Arsenic (AS)	....	.....	......	....	0.01	....	....	0.05	0.05	0.05
Barium (Ba)	....	.....	......	....	....	....	....	b	b	1.0
Cadmium (Cd)	....	.....	......	....	....	....	....	....	....	0.01
Carbon chloroform extract (CCE)	....	.....	......	....	0.2					
Chloride (Cl)	....	250	250	250	250					
Chromium, hexavalent (Cr^{+6})	....	.....	......	....	....	....	....	b	0.05	0.05

Copper (Cu)	....	.....	3.0	3.0	1.0	....	0.2			
Cyanide (CN)	....	.....	......	....	0.01	....	....	....	....	0.2
Fluoride (F)	....	.....	......	....	0.8–1.7[c,d]	....	....	1.0	1.5	1.4–2.4[c]
Iron (Fe)	....	0.3	[e]	[e]	0.3					
Lead (Pb)	....	.....	......	....	....	....	0.1	0.1	0.1	0.05
Manganese (Mn)	....	.....	[e]	[e]	0.05					
Magnesium (Mg)	....	100	125	125	....					
Nitrate (NO_3)	....	.....	......	....	45[f]					
Phenols	....	.....	0.001	0.001	0.001					
Selenium (Se)	....	.....	......	....	....	....	....	0.05	0.05	0.01
Silver (Ag)	....	.....	......	....	....	....	....	....	....	0.05
Sulfate (SO_4)	....	250	250	250	250					
Zinc (Zn)	....	....	15	15	5	....	5.0			

D. Radioactivity, μμc/l
(Recommended limit[g])

Substance	1914	1925	1942	1946	1962
Radium 226 (Ra^{226})	....	....	....	....	3
Strontium 90 (Sr^{90})	....	....	....	....	10
Gross beta activity	....	....	....	....	1,000[h]
Alpha emitters	....	....	....	....	....

[a] Filtered water only.

[b] Not to be allowed in water in distribution system.

[c] Dependent on annual average maximum daily air temperature over not less than a 5-year period.

[d] Where fluoridation is practiced, minimum recommended limits are also specified.

[e] Iron plus manganese should not exceed 0.3 mg/l.

[f] If NO_3 concentration exceeds 45 mg/l, public should be warned against use of water for infant feeding.

[g] Water supplies containing concentrations in excess of these limits will be approved if surveillance of total intakes of radioactivity from all sources indicates that such intakes are within the limits recommended by the Federal Radiation Council for control action (Chap. 13).

[h] In absence of strontium 90 and alpha emitters.

The European Standards for Drinking Water resulted from the cooperative effort, promoted by the World Health Organization in collaboration with member governments and with the assistance of experts from participating countries, to develop minimal standards of chemical and bacteriological quality which should be expected of public water supplies and to provide detailed descriptions of approved methods for their examination.

The World Health Organization's International Standards for Drinking Water are applicable under the International Sanitary Regulations for determining acceptability of water supplies at airports and other ports. They are minimal standards prepared with due consideration of the level of economic development and technological capabilities of the various countries. Five nations have adopted them as their official water quality standards, and they have served as the basis for the standards developed by several other nations.

To upgrade the water industry and to better serve the public, the AWWA through its Board of Directors approved the report of Task Group 2640P, entitled "Quality Goals for Potable Water."[41] This report defines goals for nontoxic quality characteristics of the water delivered to the consumer. These goals are more restrictive than those of the Public Health Service Standards. They are attainable within the technical competency of present practice. Public water utilities should adopt quality criteria against which they can gauge the effectiveness of their day-to-day operations.

The bacteriological, chemical, and physical requirements and recommendations for these three drinking water standards and the AWWA goals are compared in Table 1-2.

Although there is considerable agreement in the water quality criteria required or recommended by the different standards, there are a few interesting areas of variance. Both the European and International Standards emphasize that samples for bacteriological examinations shall be taken from the water at each location where it enters the distribution system. The European Standards note that such samples should be essentially free from coliform bacteria. The European Standards also recommend daily bacterial examination of the effluent from any water-treatment facility and add that "absence of such control in many small plants is to be regretted."

Both of these standards also require bacteriological examinations of samples taken from the distribution system. The bacteriological requirements applied to such samples by the European Standards are slightly less stringent than those applied to the water entering the distribution system.

The International Standards have different bacteriological requirements for treated and untreated waters, and permit relatively high coliform densities, provided not more than 40 per cent of the coliform organisms are found to be fecal coliform bacteria, in the untreated waters.

The AWWA Water Quality Goals for Potable Water defer to the U.S.

TABLE 1-2 Comparison of Various Drinking Water Standards

U.S. Public Health Service, 1962	World Health Organization, European, 1961		World Health Organization, International, 1963		AWWA Recommended Potable Quality Water Goals,[a] 1968
Water from the distribution system	Water entering the distribution system	Water from the distribution system	Treated water	Untreated water[b]	Water from the distribution system
A. Bacteriological Characteristics					
Dilution technique, five 10-ml portions	Dilution technique, five 10-ml portions		Dilution technique, five 10-ml portions		Dilution technique, five 10-ml portions
1. Not more than 10% of all portions examined each month shall show presence of coliform bacteria (coliform MPN $\overline{<}$ one per 100 ml) 2. No two consecutive samples taken from the same location, and not more than 5% of all samples examined each month, shall show presence of coliform bacteria in three or more of the five portions			1. Not more than 10% of all samples examined throughout the year shall show presence of coliform bacteria, or the annual arithmetical mean MPN shall not exceed one per 100 ml 2. None of the samples examined should show presence of coliform bacteria in more than three of the five portions examined 3. No two consecutive samples taken from the same location shall show presence of coliform bacteria in three or more of the five portions examined	1. Not more than 10% of all samples examined throughout the year shall show presence of coliform bacteria in more than three of the five portions examined (see fecal coliform) 2. None of the samples examined shall show presence of coliform bacteria in all five portions examined 3. No two consecutive samples taken from the same location shall show presence of coliform bacteria in four or more of the five portions examined	No coliform organisms

TABLE 1-2 Comparison of Various Drinking Water Standards *(Continued)*

U.S. Public Health Service, 1962	World Health Organization, European, 1961		World Health Organization, International, 1963		AWWA Recommended Potable Quality Water Goals,[a] 1968
Water from the distribution system	Water entering the distribution system	Water from the distribution system	Treated water	Untreated water[b]	Water from the distribution system
			A. Bacteriological Characteristics *(Continued)*		
Dilution technique, five 100-ml portions	Dilution technique, one 100-ml portion		Dilution technique, 100-ml portions		Dilution technique, 100-ml portions
1. Not more than 60% of all portions examined each month shall show presence of coliform bacteria (coliform bacteria MPN $\overline{<}0.9$ per 100 ml) 2. No two consecutive samples taken from the same location, and not more than 20% of all samples examined each month shall show presence of coliform bacteria in all five portions examined	None of the 100-ml samples examined shall show presence of coliform bacteria	1. Not more than 5% of all 100-ml samples examined during the year shall show presence of coliform bacteria (coliform MPN $\overline{<}0.06$ per 100 ml) 2. No two consecutive samples shall show presence of coliform bacteria			No coliform organisms

TABLE 1-2 Comparison of Various Drinking Water Standards *(Continued)*

MF technique, using 50, 100, 200, or 500 ml	MF technique	MF technique, 100 ml		MF technique
1. The arithmetic mean coliform bacterial count of all samples examined during any month shall not exceed one per 100 ml 2. The coliform count per sample shall not exceed three per 50 ml, four per 100 ml, seven per 200 ml, or 13 per 500 ml in two consecutive samples taken from the same location, nor in more than 5% of all samples examined during any month		1. The arithmetic mean coliform bacterial count of all samples examined throughout the year shall be less than one per 100 ml 2. The MF coliform count shall not exceed four per 100 ml in any two consecutive samples or in more than 10% of all samples examined during the year	1. The arithmetic mean coliform bacterial count of all samples examined throughout the year shall be less than 10 per 100 ml 2. The coliform count shall not exceed 20 per 100 ml in any two consecutive samples *Fecal coliform* Not more than 40% of the coliform index shall be found to be fecal coliform bacteria	No coliform organisms

TABLE 1-2 Comparison of Various Drinking Water Standards *(Continued)*

B. Physical Characteristics

Criterion	U.S. Public Health Service, 1962		World Health Organization, European, 1961		World Health Organization, International, 1963			AWWA Recommended Potable Quality Water Goals,[a] 1968
	Recommended limit[c]	Tolerance limit[c]	Recommended limit[c]	Tolerance limit[c]	Recommended limit[c]	Acceptable limit[c]	Tolerance Limit[c]	
Color, units	15	....	....	....	5	50	....	<3
Odor, threshold number	3, inoffensive	....	....	....	Unobjectionable	....	....	No odor
Residue:								
Filtrable, mg/l	500	....	....	....	....	....	....	<200
Nonfiltrable, mg/l	....	....	....	....	....	....	....	Virtually suspension-free
Total, mg/l	....	....	....	....	500	1,500		
Taste	Inoffensive	....	....	....	Unobjectionable	....	....	None objectionable
Turbidity, units	5	....	....	....	5	25	....	<0.1

C. Chemical Constituents, mg/l

Substance	U.S. Public Health Service, 1962		World Health Organization, European, 1961		World Health Organization, International, 1963			AWWA Recommended Potable Quality Water Goals,[a] 1968
	Recommended limit[c]	Tolerance limit[c]	Recommended limit[c]	Tolerance limit[c]	Recommended limit[c]	Acceptable limit[c]	Tolerance limit[c]	
Alkyl benzene sulfonate (ABS)	0.5	....	....	.....	0.5	1.0	....	<0.2
Aluminum (Al)	....	....	....	.....	....	......	....	<0.05
Ammonia	....	....	0.5					
Arsenic (As)	0.01	0.05	....	0.2	....	......	0.05	
Barium (Ba)	....	1.0	....	.....	....	......	1.0	
Cadmium (Cd)	....	0.01	....	0.05	....	......	0.01	
Calcium (Ca)	....	....	....	.....	75	200		
Carbon alcohol extract (CAE)	....	....	....	.....	....	......	....	<0.1
Carbon chloroform extract (CCE)	0.2	....	....	.....	0.2	0.5[d]	....	<0.04
Carbon dioxide, free (CO_2)	....	....	0					
Chloride (Cl)	250	....	350	.....	200	600		
Chromium, hexavalent (Cr^{+6})	....	0.05	....	0.05	....	......	0.05	......
Copper (Cu)	1.0	....	3.0[e]	.....	1.0	1.5	....	<0.2

Cyanide (CN)	0.01	0.2	....	0.01	....	......	0.2	
Fluoride (F)	0.8–1.7[f,g]	1.4–2.4[f]	1.5	.....	....	1.0–1.5		
Hardness (as $CaCO_3$)	....	....	100–500[h]	.....	....	....	....	80–100
Hydrogen ion concentration (pH)	....	....	....	.....	7.0–8.5[h]	6.5–9.2[h]		
Iron (Fe)	0.3	....	0.1	0.3[i]	0.3	1.0	....	<0.05
Lead (Pb)	....	0.05	0.1	0.3[j]	....	......	0.05	
Magnesium (Mg)	....	....	125[k]	.....	50	150		
Magnesium + sodium sulfate	....	....	....	.....	500	1,000		
Manganese (Mn)	0.05	....	0.1	.....	0.1	0.5	....	<0.01
Nitrate (NO_3)	45	....	50	.....	....	45		
Oxygen, dissolved (O_2)	....	....	≥ 5[l]					
Phenolic compounds (as phenol)	0.001	....	0.001	.....	0.001	0.002		
Selenium (Se)	....	0.01	....	0.05	....	......	0.01	
Silver (Ag)	....	0.05						
Sulfate (SO_4)	250	....	250	.....	200	400		
Zinc (Zn)	5	....	5	.....	5	15	....	<1.0

D. Radioactivity, $\mu\mu c/l$

Substance	U.S. Public Health Service 1962 Recommended limits[m]	World Health Organization, European, 1961 Recommended limits	World Health Organization, International, 1963 Tentative limits	AWWA Recommended Potable Quality Water Goals,[a] 1968
Radium 226 (Ra^{226})	3	....	10	
Strontium 90 (Sr^{90})	10	....	30	
Gross beta activity	1,000[n]	10[n]	1,000[o]	<100
Alpha emitters	.....	1[o]		

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[a] Not a public health standard but desirable consumer goals.

[b] If communal supplies which are distributed without treatment or disinfection cannot be maintained to the bacteriological standard established for treated and disinfected water, steps should be taken to institute chlorination, disinfection, or other treatment of the water.

[c] Recommended limit:

TABLE 1-2 Comparison of Various Drinking Water Standards *(Continued)*

(1) USPHS—concentrations which should not be exceeded where more suitable water supplies are available.
(2) WHO, European—concentrations above which may give rise to aesthetic and other troublesome problems.
(3) WHO, International—concentrations which are generally satisfactory to the consumer.
Acceptable limit:
(1) WHO, International—concentrations above which the potability of the water would be "markedly" impaired.
Tolerance limit:
(1) USPHS—concentrations above which shall constitute grounds for rejection of the supply.
(2) WHO, European—concentrations above which are likely to give rise to actual danger to health.
(3) WHO, International—concentrations above which may give rise to actual danger to health.

[d] Concentrations in excess of 0.2 mg/l indicate need for additional analyses to determine the causative agent.

[e] Recommended limit is 0.05 mg/l for water entering the distribution system; 3.0 after 16-hr contact with new pipes.

[f] Dependent on annual average maximum daily air temperature over not less than a 5-yr period.

[g] Where fluoridation is practiced, minimum recommended limits are also specified.

[h] Range, minimum to maximum limits.

[i] In larger installations where removal of iron is economic, water entering the distribution system should not contain more than 0.1 mg/l.

[j] Upper limit should be 0.1 mg/l; 0.3 permitted after 16-hr contact with lead pipes.

[k] Not more than 30 mg/l if the sulfate content equals or exceeds 250 mg/l.

[l] Minimum concentration.

[m] Water supplies containing concentrations in excess of these limits will be approved if surveillance of total intakes of radioactivity from all sources indicates that such intakes are within the limits recommended by the Federal Radiation Council for control action (see Chap. 13).

[n] In absence of strontium 90 and alpha emitters.

[o] A water with higher radioactivity may be safe for use if radiochemical analyses confirm the absence of the more dangerous radionuclides.

Public Health Service Standards for criteria that primarily and principally concern health, but focus attention on those aesthetic and other characteristics which are readily detectable by the consumers. These criteria include clarity, taste, odor, hardness, color, temperature, and staining and corrosive properties. When water meets these goals, household chores are lightened and the public health is enhanced.

Acceptance of Standards in the United States

At the present time, under federal law, the Public Health Service Drinking Water Standards are applicable only to approximately 800 municipal water supplies which provide water for loading on common carriers operating interstate or which are otherwise subject to federal quarantine regulations. However, the endorsement of these standards by the American Water Works Association and their adoption, with or without minor modifications, by most state departments of health, have resulted in general acceptance by all public supplies throughout this country. Thus, without the application of unusual pressure, these standards have been adopted voluntarily by the waterworks industry. It is rather striking to note that these standards have also materially influenced the standards promoted by the World Health Organization as well as those adopted by other countries.

Originally, it was feared that the adoption of standards involving finite values would slow down or even completely stop all progress in the field of water purification. Such prognostications have not been the experience. It was also predicted that when maximum values were proposed as a standard, operators would accept it as a license to permit degradation of the water to that quality level. Such situations have not been the case; operators of filtration plants, especially those serving the larger communities, constantly strive to produce water better than that defined by public health standards. The smaller systems, which comprise a large majority of the waterworks in the United States, frequently find it difficult to provide water complying with established standards. In fact, many small public water supplies fail to meet all aspects of the quality standards on a continuous basis. It is here where much effort is being made to establish better control and management of the water supplies. Today, it is easy to see that the adoption of standards was a perfectly logical and straightforward development which was predestined to be a successful undertaking. But, to the gentlemen who initiated the standards, credit is due for the courage displayed in taking that initial step in the light of the diverse opinions which were prevalent at the time.

INDUSTRIAL WATER SUPPLIES

Industry uses water as an ingredient in a finished product, as a buoyant transporting medium, as a cleaning agent, as a coolant, and as a source from which to obtain steam for heating and power production. The quality requirements for industrial process waters vary greatly with the type of industry and the function of the water. It is not possible to set a single standard of quality for water used for varied industrial purposes.

Quality requirements for industrial water supplies frequently exceed certain specified requirements for public supplies. Because of their need for large volumes of water meeting specific quality requirements, many industries find it economical to develop their own supply, providing such treatment as they consider desirable. Other industries and commercial establishments utilize the public supply with supplemental treatment to produce water having the desirable properties. On the other hand public water supplies are used without treatment in residential water heaters and boilers, for air conditioning of buildings, for manufacture of ice, and for many industrial purposes. Although it is impractical to provide a public water supply having the properties desired by many industrial and commercial establishments, waterworks personnel should be interested and concerned with industrial water quality requirements.

The literature contains numerous articles concerned with problems resulting from the presence of impurities in waters used for industrial purposes. Several of these publications contain recommendations pertaining to the amounts of certain impurities that may be present in water utilized by a given industry or industrial process. The publication *Water Quality Criteria*,[42] which presents an extensive review of the subject, has been the principal source of the information shown in Table 1-3. For convenience in comparing the quality requirements of industrial and public water supplies, this table includes applicable quality requirements or recommendations for drinking water.

In general the quality criteria for water used by each industry is the recommended maximum concentration of the impurity. This is true even though a range in values may be shown. Such ranges in recommended maximum values are the result of differences in opinion of two or more authorities and of differences in the processes used or products made by a given type of industry. In the few cases where minimum recommended values are given, they are so noted.

As previously noted, some industrial processes require special consideration as regards impurities in water. Water approaching the quality of distilled water is desirable for such industrial uses as high-pressure boiler-feed water, washing of aluminum hydrate in the production of metallic aluminum, in the manufacture of monochrome television picture tubes, for processing pharmaceuticals, and in baking of certain cakes and crackers.

The food, paper and pulp, and textile industries may require water having a biological quality exceeding that of drinking water. The presence of saprophytic organisms, such as chromobacteria and pseudomonas,

TABLE 1-3 Ranges in Recommended Limiting Concentrations for Industrial Process Waters (Except as noted, units are mg/l)

Use	Turbidity, units	Color, units	Taste and odor threshold	Dissolved solids	Hardness, as $CaCO_3$	Alkalinity, as $CaCO_3$	pH, units	Chlorides, as Cl	Sulfates, as SO_4	Iron, as Fe	Manganese, as Mn	Iron plus manganese	Hydrogen sulfide	Fluorides, as Fl	Other requirements
Air conditioning	.....	.....	Low	.....	.....	.....	.....	.....	...	0.5	0.5	0.5	.....	.....	Not corrosive or slime-promoting
Baking	10	10	None-low	.....	[a]	.....	.....	.....	...	0.2	0.2	0.2	0.2	.....	Potable
Boiler feed							See Chap. 16								Potable if steam is used for food preparation
Brewing	0-10	0-10	None-low	500-1,500[b]	[c]	75-80[d]	6.5-7.0[e]	60-100	...	0.1	0.1	0.1	0.2	1.0	Potable; numerous other requirements
Carbonated beverages	1-2	5-10	None-low	850	200-250	50-130	.....	250	250	0.1-0.2	0.2	0.1-0.4	0-0.2	0.2-1.0	Potable; COD, 1.5; organic matter, infinitesimal; algae and protozoa, none
Confectionery	.....	.....	Low	50-100	Soft	.....	>7.0	.....	...	0.2	0.2	0.2	0.2	.....	Potable
Cooling							See Chap. 16								
Dairy	.....	None	None	500[f]	180	.....	.....	30-	60	0.1-0.3	0.03-0.1	.....	.....	.....	Potable; NO_3-N, 5.5; NO_2-N, 0; NH_3N, trace only; COD as $KMnO_4$, 12
Drinking	5	15	3, inoffensive	500	.....	.....	.....	250	250	0.3	0.05	.....	.....	1.4-2.4[g]	Potable. See appendix to this chapter
Food canning and freezing	1-10	.....	None-low	850	[h]	30-250	$\geq$7.5	.....	...	0.2	0.2	0.2-0.3	1.0	1.0	Potable; free from saprophytic organisms; NaCl, 1,000-1,500; NO_3-N, 2.8; NH_3-N, 0.4
Food equipment, washing	1	5-20	None	850	10	.....	.....	250	...	.....	.....	0.1	.....	1.0	Potable; organic matter, infinitesimal
Food processing, general	1-10	5-10	Low	850	10-250	30-250	.....	.....	...	0.2	0.2	0.2-0.3	.....	1.0[i]	Potable
Ice manufacture	5	5	Low	170-1,300	.....	.....	.....	.....	...	0.2	0.2	0.2	.....		Potable; SiO_2, 10
Laundering	.....	.....	.....	.....	0-50	60	6.0-6.8[e]	.....	...	0.2-1.0	0.2	0.2-1.0			
Paper and pulp, fine	10	5	.....	200	100[j]	75	.....	.....	...	0.1	0.05	.....	.....	.....	Soluble SiO_2, 20; free CO_2, 10; residual Cl_2, 2
Paper, groundwood	50[k]	30	.....	500	200	150	.....	75	...	0.3	0.1	.....	.....	.....	Soluble SiO_2, 50; free CO_2 10
Paper, kraft, bleached	40	25	.....	300	100	75	.....	200	...	0.2	0.1	.....	.....	.....	Soluble SiO_2, 50; free CO_2 10
Paper, kraft, unbleached	100	100	.....	500	200	150	.....	200	...	1.0	0.5	.....	.....	.....	Soluble SiO_2, 100; free CO_2 10
Paper, soda and sulfate pulps	25[k]	5	.....	250	100[l]	75	.....	75	...	0.1	0.05	.....	.....	.....	Soluble SiO_2, 20; free CO_2 10

TABLE 1-3 Ranges in Recommended Limiting Concentrations for Industrial Process Waters (Except as noted, units are mg/l) *(Continued)*

Use	Turbidity, units	Color, units	Taste and odor threshold	Dissolved solids	Hardness, as $CaCO_3$	Alkalinity, as $CaCO_3$	pH, units	Chlorides, as Cl	Sulfates, as SO_4	Iron, as Fe	Manganese, as Mn	Iron plus manganese	Hydrogen sulfide	Fluorides, as Fl	Other requirements
Rayon and acetate fiber pulp production	5	5	....	100[f]	8	50–75	......	.....	...	0.05	0.03	0.05	.....	......	Al_2O_3, 8; Si, 25; Cu, 5
Rayon manufacture	0.3	......	....	....	55	....	7.8–8.3	.....	...	0.0	0.0	0.0			
Sugar	.....	......	....	Low	Low	....	......	20	20	0.1	....	.....	.....	......	Ca, 20; Mg, 10; bicarbonate, as $CaCO_3$, 100; sterile, no saprophytic organisms
Tanning	20	10–100	....	....	50–500	130	6.0–8.0	.....	...	0.1–0.2	0.1–0.2	0.2	.....	......	Bicarbonate hardness, low
Textile	0.3–25	0–70	....	....	0–50	....	......	100	100	0.1–1.0	0.05–1.0	0.2–1.0	.....	......	COD, 8; heavy metals, none; Ca, 10; Mg, 5; bicarbonate, as $CaCO_3$, 200

[a] Some calcium is necessary for yeast action. Too much hardness retards fermentation, but too little softens the gluten to produce soggy bread. Water of zero hardness is required for some cakes and crackers.

[b] Not more than 300 mg/l of any one substance.

[c] $CaSO_4$ less than 100 to 500 mg/l; $MgSO_4$ less than 50 to 200 mg/l.

[d] For dark beer alkalinity as $CaCO_3$ may be 80 to 150 mg/l.

[e] Range, lower to upper limits.

[f] Total solids.

[g] Tolerance limit depends on annual average of maximum daily air temperatures for a minimum of 5 years.

[h] For legumes, 25 to 75; for fruits and vegetables, 100 to 200; for peas, 200 to 400.

[i] 1.5 mg/l of fluoride has been reported to cause embrittlement and cracking of ice.

[j] Calcium hardness, 50.

[k] No gritty material.

[l] Calcium hardness, 50; magnesium hardness, 50.

may cause spoilage of food or destruction of saccharose. Nonpathogenic bacteria, algae, or fungi may adversely affect the quality of certain textiles and papers.

Although the industrial water requirements as regards turbidity, color, taste, and odor are not in conflict with those of public water supplies, the food and carbonated beverage industries frequently provide supplemental taste and odor treatment to assure the quality of their products.

Hard water affects many industrial uses. Scale deposits interfere with heat exchange in boiler and water-cooling systems. Hard water wastes soap and results in deposits of curd on textile and laundered goods. It may result in precipitation of calcium and magnesium salts in sugar. In the food industry it may cause loss in ascorbic acid and deposition of calcium during the blanching of peas and string beans. However, brewers prefer water containing considerable hardness. In some cases they even add calcium chloride and sulfate to assure optimum enzyme reaction during mashing. Too little hardness affects the baking of bread, as it softens the gluten and results in soggy bread.

Iron and manganese are probably the most important of the other water quality criteria. Excessive amounts may affect taste and color of food and beverages and cause discoloration of fabrics.

For more complete information, reference should be made to published articles on water quality requirements for the particular industry involved. *Water Quality Criteria*, together with the references noted therein, will provide substantial information.

APPENDIX

USPHS Drinking Water Standards, 1962

A revised version of the 1946 U.S. Public Health Service Drinking Water Standards was published in the August, 1961, issue of the *Journal of the American Water Works Association* under the title "Drinking Water Standards, 1961." Federal approval routine was completed by publication in the *Federal Register* for Mar. 6, 1962 (pp. 2152–2155), effective 30 days thereafter. (Because of the 1962 approval date, the standards will in the future be referred to as the "1962 standards" rather than as the "1961 standards.")

The wording of the approved document is the same as that published in the August, 1961, *Journal* except for the section on limits of radioactivity, where Sec. 6.2 and 6.21 of the following text replace Sec. 6.2 and 6.21 of the August, 1961, version.

PREFACE BY ADVISORY COMMITTEE

Domestic water supplies should protect the health and promote the well-being of individuals and the community. In this report on the revision of the 1946 edition of the USPHS drinking water standards, the objective of the committee is to recommend minimum requirements for reaching these goals.

The USPHS drinking water standards were first adopted in 1914 to protect the health of the traveling public. The general and widespread use of these standards since that time has led to a series of revisions which have been applicable to water supplies generally. The development of atomic energy and other technological advances require that these standards again be revised. To carry out this revision, the chief sanitary engineer of USPHS appointed the undersigned advisory committee. A technical subcommittee of USPHS officers and a toxicological task force were established to collect information and prepare suggestions for the consideration of the advisory committee.

In preparing this report on the revision of the standards, the committee established the following guidelines:

1. The proposed standards should be discussed widely, and due cognizance should be given to international and other standards of water quality before a final report is submitted.
2. A new section on radioactivity should be added.
3. Greater attention should be given to the chemical substances being encountered increasingly, in both variety and quantity, in water sources.
4. In establishing limits for toxic substances, intake from food and air should be considered.
5. The rationale employed in determining the various limits should be included in an appendix.
6. The proposed format, with the exceptions noted above, should not differ greatly from the present standards.
7. The standards should be generally acceptable and should be applicable to all public water supplies in the United States, as well as to those supplies used by carriers subject to USPHS regulations.
8. The following two types of limits used in previous editions should be continued:
   - *a.* Limits which, if exceeded, shall be grounds for rejection of the supply. Substances in this category may have adverse effects on health when present in concentrations above the limit.
   - *b.* Limits which should not be exceeded whenever more suitable supplies are, or can be made, available at reasonable cost. Substances in this category, when present in concentrations above the

limit, are either objectionable to an appreciable number of people or exceed the levels required by good water quality control practices.

9. These limits should apply to the water at the free-flowing outlet of the ultimate consumer.

This revision of the drinking water standards includes, for the first time, limiting concentrations of radioactivity in water. The effects on large population groups of chronic exposure to low levels of radioactivity are not yet well defined. The limits presented herein are an effort to derive conservative values from the best information now available and may be adjusted upward or downward as new and better data become available.

The committee has taken cognizance of the growing problem of potentially harmful chemicals in sources of drinking water. Limits for several new chemicals have been added, including a gross limit for the concentration of some types of synthetic chemicals. It was not feasible, however, to include limits for all the many chemicals that have varying degrees of toxic potential. Consideration was given to the more common chlorinated hydrocarbon and organophosphate insecticides, but the information available was not sufficient to establish specific limits for these chemicals. Moreover, the concentrations of these chemicals, where tested, have been below those which would constitute a known health hazard. The committee believes that pollution of water supplies with such contaminants can become significant and urges that the problem be kept under closer surveillance. Further, the committee recommends that regulatory actions be taken to minimize concentrations of such chemicals in drinking water.

In view of the accelerating pace of new developments affecting water quality, the committee recommends that a mechanism be established for continual appraisal and appropriate revision of the standards. It also recommends that USPHS intensify its continuing studies toward the development of basic information on the relationship of the biological, chemical, physical, and radiological aspects of water quality to health.

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DRINKING WATER STANDARDS

1. Definition of Terms

The terms used in these standards are as follows:

1.1. *Adequate protection by natural means* involves one or more of the following processes of nature that produce water consistently meeting the requirements of these standards: dilution, storage, sedimentation, sunlight, aeration, and the associated physical and biological processes which tend to accomplish natural purification in surface waters and, in the case of ground waters, the natural purification of water by infiltration through soil and percolation through underlying material and storage below the ground water table.

1.2. *Adequate protection by treatment* is any one or any combination of the controlled processes of coagulation, sedimentation, sorption, filtration, disinfection, or other processes which produce a water consistently meeting the requirements of these standards. This protection also includes processes which are appropriate to the source of supply; works which are of adequate capacity to meet maximum demands without creating health hazards, and which are located, designed, and constructed to eliminate or prevent pollution; and conscientious operation by well trained and competent personnel whose qualifications are commensurate with the responsibilities of the position and acceptable to the reporting agency and the certifying authority.

1.3. *Certifying authority* is the surgeon general of USPHS or his duly authorized representatives. (Reference to the certifying authority is applicable only for those water supplies to be certified for use on carriers subject to the USPHS regulations—42 CFR Part 72.)

1.4. The *coliform group* includes all organisms considered in the coliform group as set forth in *Standard Methods for the Examination of Water and Wastewater,* current edition [11th ed., 1960], prepared and published jointly by the American Public Health Association, American Water Works Association, and Water Pollution Control Federation.

1.5. *Health hazards* are conditions, devices, or practices in the water supply system and its operation which create, or may create, a danger to the health and well-being of the water consumer. An example of a health hazard is a structural defect on the water supply system, whether of location, design, or construction, which may regularly or occasionally prevent satisfactory purification of the water supply or cause it to be polluted from extraneous sources.

1.6. *Pollution,* as used in these standards, is defined as the presence of any foreign substance (organic, inorganic, radiological, or biological) in water which tends to degrade its quality so as to constitute a hazard or impair the usefulness of the water.

1.7. *Reporting agencies* are the respective official state health agencies or their designated representatives.

1.8. *The standard sample* for the bacteriological test shall consist of:

1.81. For the bacteriological fermentation tube test, five standard portions of either: *(a)* 10 ml or *(b)* 100 ml

1.82. For the membrane filter technique, not less than 50 ml

1.9. *Water supply system* includes the works and auxiliaries for collection, treatment, storage, and distribution of the water from the sources of supply to the free-flowing outlet of the ultimate consumer.

2. Source and Protection

2.1. The water supply should be obtained from the most desirable source feasible, and effort should be made to prevent or control pollution of the source. If the source is not adequately protected by natural means, the supply shall be adequately protected by treatment.

2.2. Frequent sanitary surveys shall be made of the water supply system to locate and identify health hazards which might exist in the system. The manner and frequency of making these surveys, and the rate at which discovered health hazards are to be removed, shall be in accordance with a program approved by the reporting agency and the certifying authority.

2.3. Approval of water supplies shall be dependent in part upon:

a. Enforcement of rules and regulations to prevent development of health hazards

b. Adequate protection of the water quality throughout all parts of the system, as demonstrated by frequent surveys

c. Proper operation of the water supply system under the responsible charge of personnel whose qualifications are acceptable to the reporting agency and the certifying authority

d. Adequate capacity to meet peak demands without development of low pressures or other health hazards

e. Record of laboratory examinations showing consistent compliance with the water quality requirements of these standards

2.4. For the purpose of application of these standards, responsibility for the conditions in the water supply system shall be considered to be held by:

a. The water purveyor, from the source of supply to the connection to the customer's service piping

b. The owner of the property served and the municipal, county, or other authority having legal jurisdiction, from the point of connection to the customer's service piping to the free-flowing outlet of the ultimate consumer

3. Bacteriological Quality

3.1. *Sampling.*

3.11. Compliance with the bacteriological requirements of these standards shall be based on examinations of samples collected at representative points throughout the distribution system. The frequency of sampling and the location of sampling points shall be established jointly by the reporting agency and the certifying authority after investigation by either agency, or both, of the source, method of treatment, and protection of the water concerned.

3.12. The minimum number of samples to be collected from the distribution system and examined each month should be in accordance with the number in Fig. *A* for the population served by the system. For the purpose of uniformity and simplicity in application, the number determined from Fig. A should be in accordance with the following: for a population of 25,000 or less, to the nearest 1; 25,001–100,000, to the nearest 5; and more than 100,000, to the nearest 10.

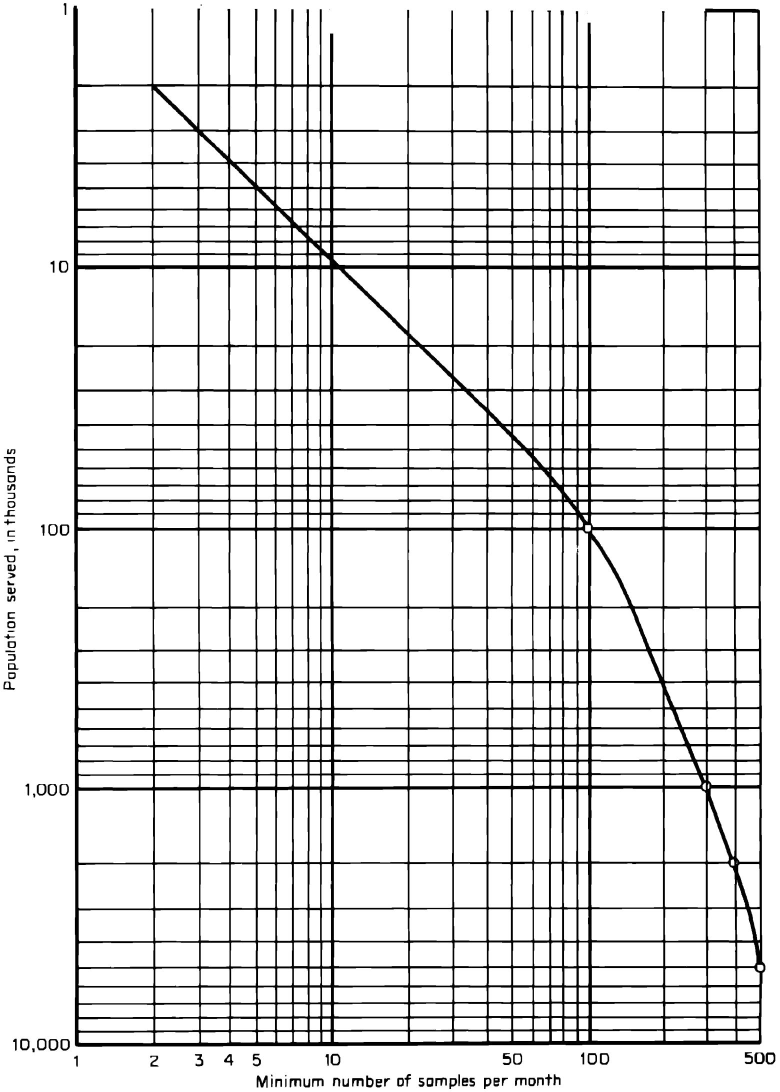

Fig. A Relation between minimum number of samples to be collected per month and population served.

3.13. In determining the number of samples examined monthly, the following samples may be included, provided all results are assembled and available for inspection, and the laboratory methods and technical competence of the laboratory personnel are approved by the reporting agency and the certifying authority:

a. Samples examined by the reporting agency

b. Samples examined by local government laboratories

c. Samples examined by the water works authority

d. Samples examined by commercial laboratories

3.14. The laboratories in which these examinations are made and the methods used in making them shall be subject to inspection at any time by the designated representatives of the certifying authority and the reporting agency. Compliance with the specified procedures and the results obtained shall be used as a basis for certification of the supply.

3.15. Daily samples collected following a bacteriologically unsatisfactory sample as provided in Sec. 3.21, 3.22, and 3.23 shall be considered as special samples and shall not be included in the total number of samples examined. Neither shall such special samples be used as a basis for prohibiting the supply, provided that:

1. When waters of unknown quality are being examined, simultaneous tests are made on multiple portions of a geometric series to determine a definitive coliform content
2. Immediate and active efforts are made to locate the cause of pollution
3. Immediate action is taken to eliminate the cause
4. Samples taken following such remedial action are satisfactory

3.2. *Limits.* The presence of organisms of the coliform group as indicated by samples examined shall not exceed the following limits:

3.21. When 10-ml standard portions are examined, not more than 10 per cent in any month shall show the presence of the coliform group. The presence of the coliform group in three or more 10-ml portions of a standard sample shall not be allowable if this occurs:

a. In two consecutive samples

b. In more than one sample per month when less than twenty are examined per month

c. In more than 5 per cent of the samples when twenty or more are examined per month

When organisms of the coliform group occur in three or more of the 10-ml portions of a single standard sample, daily samples from the same sampling point shall be collected promptly and examined until the results obtained from at least two consecutive samples show the water to be of satisfactory quality.

3.22. When 100-ml standard portions are examined, not more than 60 per cent in any month shall show the presence of the coliform group. The presence of the coliform group in all five of the 100-ml portions of a standard sample shall not be allowable if this occurs:

a. In two consecutive samples

b. In more than one sample per month when less than five are examined per month

c. In more than 20 per cent of the samples when five or more are examined per month

When organisms of the coliform group occur in all five of the 100-ml portions of a single standard sample, daily samples from the same sampling point shall be collected promptly and examined until the results obtained from at least two consecutive samples show the water to be of satisfactory quality.

3.23. When the membrane filter technique is used, the arithmetic mean coliform density of all standard samples examined per month shall not exceed one per 100 ml. Coliform colonies per standard sample shall not exceed three per 50 ml, four per 100 ml, seven per 200 ml, or thirteen per 500 ml in:

a. Two consecutive samples

b. More than one standard sample when less than twenty are examined per month

c. More than 5 per cent of the standard samples when twenty or more are examined per month

When coliform colonies in a single standard sample exceed the above values, daily samples from the same sampling point shall be collected promptly and examined until the results obtained from at least two consecutive samples show the water to be of satisfactory quality.

TABLE 1*

Substance	*Concentration, mg/l*
Alkyl benzene sulfonate (ABS)	0.5
Arsenic (As)	0.01
Chloride (Cl)	250.0
Copper (Cu)	1.0
Carbon chloroform extract (CCE)	0.2
Cyanide (CN)	0.01
Fluoride (F)	†
Iron (Fe)	0.3
Manganese (Mn)	0.05
Nitrate (NO_3)‡	45.0
Phenols	0.001
Sulfate (SO_4)	250.0
Total dissolved solids	500.0
Zinc (Zn)	5.0

*Refer to Sec. 5.21.

†See Sec. 5.23.

‡In areas in which the nitrate content of water is known to be in excess of the listed concentration, the public should be warned of the potential dangers of using the water for infant feeding.

4. Physical Characteristics

4.1. *Sampling.* The frequency and manner of sampling shall be determined by the reporting agency and the certifying authority. Under normal circumstances, samples should be collected one or more times per week from representative points in the distribution system and examined for turbidity, color, threshold odor, and taste.

4.2. *Limits.* Drinking water should contain no impurity which would cause offense to the sense of sight, taste, or smell. Under general use, the following limits should not be exceeded: turbidity, 5 units; color, 15 units; and threshold odor number, 3 units.

5. Chemical Characteristics

5.1. *Sampling.* The frequency and manner of sampling shall be determined by the reporting agency and the certifying authority. Under normal circumstances, analyses for substances listed below need be made only semiannually. If, however, there is some presumption of unfitness because of the presence of undesirable elements, compounds, or materials, periodic determinations for the suspected toxicant or material should be made more frequently, and an exhaustive sanitary survey should be made to determine the source of the pollution. Where the concentration of a substance is not expected to increase in processing and distribution, available and acceptable source water analyses performed in accordance with standard methods may be used as evidence of compliance with these standards.

Where experience, examination, and available evidence indicate that particular substances are consistently absent from a water supply or below levels of concern, semiannual examinations for those substances may be omitted when approved by the reporting agency and the certifying authority.

TABLE 2*

Substance	*Concentration, mg/l*
Arsenic (As)	0.05
Barium (Ba)	1.0
Cadmium (Cd)	0.01
Chromium (Cr^{6+})	0.05
Cyanide (CN)	0.2
Fluoride (F)	†
Lead (Pb)	0.05
Selenium (Se)	0.01
Silver (Ag)	0.05

*Refer to Sec. 5.22.

†See Sec. 5.23.

The burden of analysis may be reduced in many cases by using data from acceptable sources. Judgment concerning the quality of water supply and the need for performing specific local analyses may depend in part on information produced by such agencies as: (1) USGS, which determines chemical quality of surface and ground waters of the United States and publishes these data in "Water Supply Papers" and other reports, and (2) USPHS, which determines water quality related to pollution (or the absence of pollution) in the principal rivers of the United States and publishes these data annually in "National Water Quality Network." Data on pollution of waters as measured by carbon chloroform extracts (CCE) may be found in the latter publication.

5.2. *Limits.* Drinking water shall not contain impurities in concentrations which may be hazardous to the health of the consumers. It should not be excessively corrosive to the water supply system. Substances used in its treatment shall not remain in the water in concentrations greater than required by good practice. Substances which may have deleterious physiological effect, or substances for which physiological effects are not known, shall not be introduced into the system in a manner which would permit them to reach the consumer.

5.21. The chemical substances shown in Table 1 should not be present in a water supply in excess of the listed concentrations where, in the judgment of the reporting agency and the certifying authority, other more suitable supplies are or can be made available.

5.22. The presence of substances in excess of the concentration listed in Table 2 shall constitute grounds for rejection of the supply.

5.23. *Fluoride.* When fluoride is naturally present in drinking water, the concentration should not average more than the appropriate upper limit shown in Table 3. Presence of fluoride in average concentrations greater than two times the optimum values in Table 3 shall constitute grounds for rejection of the supply.

Where fluoridation (supplementation of fluoride in drinking water) is practiced, the average fluoride concentration shall be kept within the upper and lower control limits shown in Table 3.

In addition to the sampling required by Sec. 5.1, fluoridated and defluoridated supplies shall be sampled with sufficient frequency to determine that the desired fluoride concentration is maintained.

6. Radioactivity

6.1. *Sampling.* The frequency of sampling and analysis for radioactivity shall be determined by the reporting agency and the certifying authority after consideration of the likelihood of significant amounts being present. Where concentrations of Ra^{226} or Sr^{90} may vary considerably, quarterly

TABLE 3*

Annual avg of max. daily air temperature,† °F	Recommended control limits for fluoride concentration, mg/l		
	Lower	Optimum	Upper
50.0–53.7	0.9	1.2	1.7
53.8–58.3	0.8	1.1	1.5
58.4–63.8	0.8	1.0	1.3
63.9–70.6	0.7	0.9	1.2
70.7–79.2	0.7	0.8	1.0
79.3–90.5	0.6	0.7	0.8

*Refer to Sec. 5.23.

†Based on temperature data obtained for a minimum of 5 years.

samples composited over a period of 3 months are recommended. Samples for determination of gross activity should be taken and analyzed more frequently.

As indicated in Sec. 5.1, data from acceptable sources may be used to indicate compliance with these requirements.

6.2. *Limits.*

6.21. The effects of human radiation exposure are viewed as harmful and any unnecessary exposure to ionizing radiation should be avoided. Approval of water supplies containing radioactive materials shall be based upon the judgment that the radioactivity intake from such water supplies when added to that from all other sources is not likely to result in an intake greater than the radiation protection guidance* recommended by the Federal Radiation Council and approved by the President. Water supplies shall be approved without further consideration of other sources of radioactivity intake of Ra^{226} and Sr^{90} when the water contains these substances in amounts not exceeding 3 and 10 $\mu\mu$c/l, respectively. When these concentrations are exceeded, a water supply shall be approved by the certifying authority if surveillance of total intakes of radioactivity from all sources indicates that such intakes are within the limits recommended by the Federal Radiation Council for control action.

6.22. In the known absence† of Sr^{90} and alpha emitters, the water supply is acceptable when the gross beta concentrations do not exceed 1,000 $\mu\mu$/l. Gross beta concentrations in excess of 1,000 $\mu\mu$c/l shall be grounds for rejection of supply except when more complete analyses indicate that

*The Federal Radiation Council, in its Memorandum for the President, Sept. 13, 1961, recommended that "routine control of useful applications of radiation and atomic energy should be such that expected average exposures of suitable samples of an exposed population group will not exceed the upper value of Range II (20 $\mu\mu$c/day of Ra^{226} and 200 $\mu\mu$c/day of Sr^{90})."

†"Absence" is taken here to mean a negligibly small fraction of the above specific limits, where the limit for the unidentified alpha emitters is taken as the listed limit for Ra^{226}.

concentrations of nuclides are not likely to cause exposures greater than the Radiation Protection Guides as approved by the President on recommendation of the Federal Radiation Council.

7. Recommended Analytical Methods

7.1. Analytical methods to determine compliance with the requirements of these standards shall be those specified in *Standard Methods for the Examination of Water and Wastewater,* APHA, AWWA, and WPCF, New York, current edition [11th ed., 1960], and those specified as follows:

7.2. *Barium.* Rainwater, F. H., and L. L. Thatcher: Methods for the Collection and Analysis of Water Samples, *USGS, Water Supply Papers, No. 1454,* Govt. Printing Office, Washington, D.C.

7.3. *Carbon Chloroform Extract (CCE).* Method for Determining the Carbon Chloroform Extract (CCE) in Drinking Water, R. A. Taft San. Eng. Center, USPHS, Cincinnati (1961).

7.4. *Radioactivity.* Laboratory Manual of Methodology; Radionuclide Analysis of Environmental Samples, *Tech. Rept. R59-6,* R. A. Taft San. Eng. Center, USPHS, Cincinnati; and Methods of Radiochemical Analysis, *Tech. Rept. 173,* Joint WHO-FAO Committee, World Health Organization (1959).

7.5. *Selenium.* Magin, G. B., et al: Suggested Modified Method for Colorimetric Determination of Selenium in Natural Water, *J. AWWA,* 52:119 (Sept., 1960).

7.6. *Organisms of the Coliform Group.* All of the details of techniques in the determination of bacteria of this group, including the selection and preparation of apparatus and media, the collection and handling of samples, and the intervals and conditions of storage allowable between collection and examination of the water sample, shall be in accordance with *Standard Methods for the Examination of Water and Wastewater,* current edition, and the procedures shall be those specified therein for:

7.61. Membrane Filter Technique, standard test, or

7.62. Completed Test, or

7.63. Confirmed Test, procedure with brilliant green lactose bile broth*

7.64. Confirmed Test, procedure with Endo or eosin methylene blue agar plates.*

AWWA RESOLUTION

Acting on behalf of the Officers and Directors, the AWWA Executive Committee adopted the resolution on the next page endorsing the 1961 revision of the USPHS Drinking Water Standards as "minimum" standards for all public water supplies.

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*The Confirmed Test is allowed, provided the value of this test to determine the sanitary quality of the specific water supply being examined is established beyond reasonable doubt by comparisons with Completed Tests performed on the same water supply.

The resolution read:

> Whereas, the 1961 Drinking Water Standards of the U.S. Public Health Service, as prepared by the Advisory Committee on Revision of U.S. Public Health Service 1946 Drinking Water Standards and promulgated for use in the administration of interstate quarantine regulations, are intended to apply only to water used on common carriers engaged in interstate commerce;
>
> Whereas, the 1961 Drinking Water Standards are to serve as minimum requirements to protect the health and promote the well-being of individuals and of communities;
>
> Whereas, it is the desire of the American Water Works Association to support all efforts to promote health through safe water supplies and to recognize reasonable standards of quality for water furnished by public water supply systems; and
>
> Whereas, it is the hope of the American Water Works Association that its acceptance of the 1961 Drinking Water Standards will establish these standards as minimum criteria of quality for all public water supplies in the United States; now, therefore, be it
>
> *Resolved:* By the Officers and Directors of the American Water Works Association, that the 1961 Drinking Water Standards of the U.S. Public Health Service be accepted as minimum standards for all public water supplies.

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2

Aeration

By G. R. SCOTT

INTRODUCTION

In water-treatment practice, the term "aeration" is applied to those processes in which water is brought into intimate contact with air for the purpose of changing the concentrations of volatile substances contained in the water.

M. N. Baker in "Quest for Pure Water"[1] states:

> In the eighteenth century, artificial aeration was directed at making up the oxygen deficiencies of distilled water and of rain water that had been stored in household cisterns. Toward the end of the eighteenth century and early in the next, aeration was applied to a few public water supplies carrying decomposed vegetable or animal matter. Not until the last half of the nineteenth century did aeration become a marked feature of municipal supplies. Even then, the number of applications was small and pertained chiefly to stored waters subject to taste and odors from algae growths. In this period, aeration was applied here and there, generally to ground waters, for the removal of iron, and then of manganese, and also to eliminate malodorous gases from sulfur-bearing ground waters.

The inventory of water treatment plants published by USPHS in 1958 lists 2,154 plants having aerators.[2] The breakdown as to type is as follows:

Cascade	762
Trays	558
Spray	200
Patented types	346
Other types	134
Unspecified	154

PURPOSE

The basic purpose of aeration is the improvement of the physical and chemical characteristics of water for domestic, commercial, and industrial use. The accomplishment of this intent requires in some cases a decrease and in others an increase in the concentrations of volatile substances in the water.

Substances that may be decreased by aeration include:

1. Substances producing tastes and odors, such as hydrogen sulfide and some volatile organic compounds.
2. Substances that increase the corrosive action of water, such as carbon dioxide and hydrogen sulfide. Although oxygen may also be considered in this category, its concentration is seldom decreased by the usual aeration processes under the conditions of temperature and pressures encountered in water-treatment plants.
3. Substances that react or interfere with chemicals used in the treatment of water. These include carbon dioxide in softening and iron removal processes and hydrogen sulfide before chlorination.
4. Miscellaneous gases, such as methane.

Substances that may be added to water by aeration include:

1. Gases from the atmosphere, particularly oxygen, which is useful in the improvement of taste and odor and for the oxidation of iron, manganese, hydrogen sulfide, and to a limited extent organic matter.
2. Substances that alter the characteristics of water in preparation for a subsequent processing step. In the recarbonation process, after softening with excess lime, carbon dioxide is added by an aeration device for the neutralization of causticity. Carbon dioxide is also added at times during aeration to waters high in sulfides in order to lower the pH value and thereby increase the volatility of hydrogen sulfide for more effective removal.

LIMITATIONS

Aeration generally is not an efficient method for the removal or reduction of unpleasant tastes and odors because most of the substances causing the undesirable traits are not sufficiently volatile. When the volatility is adequate, however, these substances can be removed by aeration.

The essential oils of algae (released as the organisms disintegrate) are not highly volatile and, hence, are not satisfactorily removed by aeration alone. Odor removals of only 50 per cent have been reported where *Synura* was the causative organism. Among those reporting that aeration alone has not been successful in the satisfactory reduction of tastes and odors caused by algae are Denver, Colorado, and the Oklahoma State University at Stillwater, Oklahoma. Others report satisfactory operation, but indicate that activated carbon is also used for taste and odor reduction. A number of plants in Ohio (Akron, Barberton, Fremont, Nelsonville, Piqua, and Wellston) have discontinued the practice because aeration either has been ineffective or has aggravated the trouble. The plants at San Diego, California; Bloomington, Illinois; and Riverdale, New Jersey, also report that the use of aerators for taste and odor reduction has been discontinued.

Tastes and odors caused by chemicals carried by some industrial wastes may be aggravated by chlorination. Although not satisfactorily reduced by direct aeration, some of these odors may disappear after storage of a few days following aeration.[3]

The most important functions of aeration are the removal of carbon dioxide from water prior to lime-soda softening and the addition of oxygen for the removal of iron and manganese. The benefits in these processes, however, are not always obtained completely without adverse effects. In some plants the oxygen entering solution during the aeration process renders the water more corrosive.[4] Lansing, Michigan, reported that while aerating well water for the reduction of carbon dioxide prior to softening and iron removal, numerous complaints of red water in hot water systems were received; after aeration was discontinued and the carbon dioxide was neutralized with lime in the regular plant treatment process, the complaints ceased and did not recur. Ann Arbor, Michigan, and LaGrange, Illinois, have also discontinued aeration in order to stop formation of red water.

Aeration alone is usually sufficient to cause precipitation of iron and manganese when organic matter is not present.[5] When such material is present, it combines with the iron and manganese to form complex compounds which do not precipitate satisfactorily after aeration. In such instances it has been found that moderate rather than vigorous aeration gives better results.

The use of aerators after treatment or as the sole treatment for well waters should be examined quite critically, particularly as the water is subjected to airborne contamination. At one plant, filtered water enters the reservoir through spray nozzles throwing the water from 12 to 14 ft into the air. During 1949, the effluent contained coliform organisms, although tests on the influent were negative. West Palm Beach, Florida, abandoned aerators because chironomids laid eggs on the surface of water in the basins and the larvae or "blood worms," after hatching, appeared at the consumer taps.

In supplies where the carbon dioxide content of the raw water is low or where other treatment processes are relied upon to remove or reduce tastes and odors, the cost of aeration should be compared with that of chemicals required to accomplish the same purpose. If the main purpose of aeration is taste and odor reduction, it is quite probable that no additional chemicals will be required when aeration is discontinued. On the other hand, additional lime will be required to neutralize the carbon dioxide that would be removed by aeration. An exception[6] to this general statement is found at Appleton, Wisconsin, where the reduction in threshold odor by aeration during August and September is about 23 units, while during October and November, when the water is colder, the reduction is from 3 to 5 units. Aeration is economical in the warmer months, but is of questionable value during October and November. Another exception is the installation at the Nitro, West Virginia, plant of West Virginia Water Service Company.[7]

About 10 ft of head is required for many of the waterfall aerators, and air must be compressed to about the same extent in the diffused-air type. The power requirements for the two types will not differ materially and, for the purpose of the following comparison, are taken as 39 kwhr per million gallons or the requirement for pumping based on 80 per cent efficiency. Theoretically, 1 mg/l of carbon dioxide requires 5.9 lb of 90% quicklime per million gallons for partial neutralization to calcium bicarbonate and 11.8 lb per million gallons for complete neutralization to calcium carbonate. If the cost of power is $0.01 per kilowatthour, the operating cost of aeration will be approximately $0.39 per million gallons. If lime costs $0.008 per pound, the cost per million gallons of removing 2 mg/l of carbon dioxide by complete neutralization is $0.094. For partial neutralization the cost would be one-half this much. If the reduction of carbon dioxide is no more than approximately 4 to 8 mg/l, it may be more economical to discontinue the use of aeration. Baylis[8] is of the opinion that where the carbon dioxide content is approximately 10 mg/l or less, it is usually more economical to neutralize with lime or soda ash than to employ aeration.

THEORY

The relative amounts of the volatile substances contained in air and water and their concentrations in water with respect to their saturation value are factors that control the rate at which the interchange takes place. Substances that occur in water in amounts less than or in excess of their saturation values are changed in concentration by aeration, with the saturation value the limit of change for both conditions.

The substances involved in the reaction must be volatile. Oxygen, carbon dioxide, and hydrogen sulfide are volatile, and their concentrations in water are readily affected by the process. Many of the taste- and odor-producing compounds occurring in water as the result of algal growths or industrial wastes are not volatile at the temperatures encountered in natural waters and cannot be removed by aeration. Since higher temperatures increase the volatility of the compounds and decrease their saturation values, aeration for the removal of volatile materials is more effective in warm than in cold waters. Similarly, the removal by aeration of some gases such as H_2S, CO_2, and NH_3 is strongly dependent upon the pH of the water. Low pH values favor the removal of these compounds by aeration.

The interchange of the substances from water to air or from air to water takes place at the air-water surface. The rate at which the interchange occurs is the result of the relative concentration of the substance at this surface and the rapidity with which new surfaces are formed and exposed. Since molecular diffusion of gases through liquids occurs at low rates which exert little effect on the efficiency of the process, all types of aerators, to be efficient, must develop and continually change large surface areas where fresh contacts are made and through which the interchange may take place.

The exchange can be described by these formulas, based on equations given by Lewis and Whitman[9] and discussed by Haney.[10]

Gas absorption:

$$C_t = S - (S - C_0)10^{-k(A/V)t} \qquad (1)$$

Gas release:

$$C_t = S + (C_0 - S)10^{-k(A/V)t} \qquad (2)$$

These formulas and the differential equations from which they are derived indicate that:

1. At any instant, the rate of gas transfer is directly proportional to the difference between the gas saturation concentration S and the actual concentration C_t in the water.

2. The rate of gas transfer is directly proportional to the ratio of the exposed area to the volume of water, A/V.

3. The rate of gas transfer is directly proportional to the gas transfer coefficient k which in turn is dependent on the diffusivity of the gas in question and the film resistance.

4. The total amount of gas transfer is greater as the time of aeration increases.

5. The percentage change in gas saturation deficit $S - C_t$ or surplus $C_t - S$ for any given time period t is constant based on the deficit or surplus at the beginning of the time period.

6. Temperature and pressure are important factors because they influence gas solubility S. Temperature also influences diffusivity and film resistance and hence the value of k.

The term C_0 is the concentration of gas originally present in the water.

There are a number of papers reporting on the general subject of aeration which contain additional information that may be of interest. Pasveer[11] reports work done at the Research Institute for Public Health Engineering (a facility of the Netherlands National Health Research Council) on the rate of solution of oxygen in water. Ippen and Carver[12] report results of investigations, supported by a research grant from the National Institutes of Health, on the rate of oxygen absorption. Camp[13] discusses gas transfer to and from aqueous solutions and presents the results of experiments carried out under his direction on diffused aeration and carbonation of mixed municipal sewage and alkaline textile wastes. O'Conner and Dobbins[14] discuss the theory of reaeration in streams and present experimental data in verification of the theoretical formulations.

DESIGN AND OPERATING DATA

The time factor and the ratio of surface area to the volume of water, A/V, are important factors that must be considered in the design of an aerator. The partial pressure or the concentration in the air of the gas to be removed must also be considered and provision made for ventilation in installations where the unit is to be housed.

Aeration equipment used in present practice employs one of two methods to control time and A/V. One method exposes water films to the air and the other introduces air in the form of small bubbles in the water. The first is generally known as the "waterfall type" and the second as the "diffused-air type."

Because waterfall aerators, as the name implies, require that the water be dropped in the process, their use results in the loss of a considerable amount of head. On the other hand, although little or no loss of head is required for the diffused-air units, they require the expenditure of energy in compressing the air and forcing it through small orifices into the water at some distance below the surface.

Difficulties in the operation of waterfall aerators can be expected from freezing during the winter in extreme climates unless they are housed. If an aerator is enclosed, careful consideration should be given to ventilation in the interest of efficiency and safety.

The work of Brown[15] at Memphis demonstrated that good ventilation is necessary for the effective removal of gases from solution. His conclusion, based on data from pilot and full-scale plant operations, was that the media in multiple-tray aerators should be so arranged that fresh air continuously passes through the falling water and over the media. He further concluded that it was impossible to secure consistent results with an aerator dependent on natural ventilation alone. Better results were obtained when a breeze was blowing than when a calm prevailed.

Ventilation for an enclosed aerator is also of importance from a safety standpoint in the case of removal of carbon dioxide, methane, and hydrogen sulfide. The first named is an asphyxiant, the second creates an explosion hazard, and the third is highly poisonous.

As corrosion of the structure and equipment represents a major consideration in the design of aerators, materials which will resist the corrosive action of the water must be used. Concrete, aluminum, asbestos cement, copper-bearing steel, stainless steel, and creosoted lumber have been used in the construction of aerators. Bronze and cast iron are used in nozzles and a number of patented devices. Ordinary steel should be used only in those locations that are readily accessible for painting at frequent intervals.

Because slime and algal growths may be troublesome in waterfall aerators of the cascade and tray types—especially if the units are located outdoors and subject to sunlight—treatment by chlorine or copper sulfate may be necessary.

WATERFALL AERATORS

1. *Spray Aerators.* Spray aerators consist of fixed nozzles on a pipe distribution grid through which the water is forced into the air as in a fountain. Spray aerators possess great public appeal and aesthetic value. They require such a large area that they cannot be housed economically, and they generally are not operated during freezing weather.

The time of exposure of each droplet of spray depends upon its initial velocity and its trajectory, while the size of the droplet (and consequently its surface area–volume ratio A/V) is a function of the dispersing action of the nozzle.

The initial velocity is given by the equation

$$V = C_v\sqrt{2\,gh} \tag{3}$$

and the discharge by the equation

$$Q = C_d\,a\sqrt{2\,gh} \tag{4}$$

in which h is the total head on the nozzle; g is the acceleration of gravity; a is the area of the opening; C_v is the coefficient of velocity; $C_d = C_v \times C_c$ is the coefficient of discharge; and C_c is the coefficient of contradiction. The coefficients of velocity, contractions, and discharge vary widely with the shape and other characteristics of the orifice or nozzle.

The trajectory of the spray may be vertical or inclined. If θ represents the angle between the initial velocity vector and the horizontal, the theoretical time of exposure of the droplet is given by the equation

$$t = 2C_v \sin\theta\sqrt{\frac{2h}{g}} \tag{5}$$

As the sine of an angle less than 90° is less than 1.0, it is apparent that the vertical jet gives the longest time of exposure for a given head. The inclined jet, however, has a longer path of travel, resulting in less interference among the falling droplets.

The design of the nozzle is extremely important in achieving optimum dispersion of the water. Nozzles vary from those having plain tips to those which impart a whirling motion to the water. Among the special designs are the rifled nozzle, the centrifugal (West Palm Beach) nozzle, impinging devices, Sacramento floating cones, and rotating reaction nozzles similar to certain lawn sprinklers.

The size, number, and spacing of the nozzles depend upon the head and the area available for aeration. Nozzles generally used are from 1 to 1½ in. in diameter, as smaller nozzles tend to clog and require excessive maintenance. The discharge ratings vary from about 75 to 175 gpm at 10 psi, and the spacing varies from 2 to 12 ft. The area required appears to range from 50 to 150 sq ft per mgd of capacity.

Although spray aerators are spectacular and provide a high surface-volume ratio in the fine droplets, the time of exposure is very short (about 2 sec for a vertical jet operating under a head of 20 ft), and this type is no more efficient than others requiring less space.

Table 2-1 lists the pertinent details of construction and gives the results of carbon dioxide removals of a number of typical spray aerators. Flentje[16] reports that, in general, spray aerators will remove from 70 to 80 per cent of carbon dioxide and that removals as high as 90 per cent have been experienced.

Not listed in Table 2-1, but worthy of mention, is the installation of the Nitro plant of the West Virginia Water Service Company, Charleston, West Virginia.[7] Threshold odors of 5,000 to 6,000 caused by industrial wastes have been encountered in the raw water. The primary aerator operates 12 to 16 hr per day with pressures at 55 psi, while the water from the collecting basin is recirculated through the sprays for the remaining 8 to 12 hr. Water is also drawn from this basin and forced through a second set of sprays at a pressure of 25 psi before going to the remainder of the treatment processes. From 97 to 99 per cent of the odors are removed by the aeration procedure, leaving a threshold odor of approximately 60 to be removed by other means.

2. *Cascade Aerators.* Many variations of cascade aerators are in use. The general principle is to spread the water as much as possible and let it flow over obstructions to produce turbulence and to change water surfaces in contact with the atmosphere. The simplest type is a concrete-step structure which spreads the water and allows it to fall from one level to another. Some commercial equipment is constructed in the form of circular trays with shallow weirs on their periphery. The water, spread in the shallow

TABLE 2-1 Typical Spray Aerators

Installation	Design capacity, mgd	Number of nozzles	Spacing, ft	Type	Pressure, psi	Space per unit of capacity, sq ft/mgd	Operating results		
							Flow, mgd	CO_2, mg/l	
								Raw	Aerated
Contra Costa, Cal.	12	42	4	Sacramento	1.64	138			
Denver, Colo., North Side Filter Plant:[a]									
Aerator 1	64	600	3	Special	11.27	85	64	Trace	0.5
Aerator 2	100	600	3	Special	6.50	54	100	Trace	0.5
Jacksonville, Fla.:[b]									
Main St.	12.95	200	2.5	Floating cone	0.98	97	7	10	4
Hendricks Ave.	7.30	26	6	Adjustable cone	1.19	129	2	8	4
West Palm Beach, Fla.[c]	20	202	2 and 3	West Palm Beach type	10	78	Variable	3.7	12.9
Bangor, Maine[d]	8	80	2–2.5	Patented	3	50	4.25	7.5	
Lawrence, Mass.[e]	10	70	10	Sacramento	1.73	700			
Springfield, Mo.[e]	5.6	39	12	Patented	17	1,000			
Appleton, Wis.[f]	8	72	3.5 × 4	Patented	2.3	128			

[a] Surface supply essentially free of carbon dioxide.

[b] Supply from deep wells, all containing hydrogen sulfide in concentrations from 1.5 to 2.0 mg/l. Aeration removes from 25 to 40 per cent and supplies oxygen for oxidation of remainder.

[c] Supply from shallow lakes. Aeration for reduction of algal odors and carbon dioxide reduction for iron removal. Alum added prior to aeration, which accounts for high carbon dioxide content of aerated water.

[d] Surface supply. Aerator for reduction of carbon dioxide and nitrogen trichloride. Aerated water contains about 15 mg/l free chlorine.

[e] Surface supply. Aerator for reduction of algal odors.

[f] Surface supply. Aerator for reduction of algal odors. Reports average reduction of threshold odor from 24 to 51 per cent. Alum added prior to aeration.

trays, flows in thin sheets over the weirs as it drops from an upper to a lower tray.

The surface area–volume ratio and the time of exposure in a cascade aerator are difficult to evaluate. The time of exposure can be extended by increasing the number of steps, and the surface area–volume ratio can be improved by adding obstructions to increase turbulence. Generally, the head required ranges from 3 to 10 ft. The cascade aerator at Champaign (Urbana, Illinois) reduces carbon dioxide from a level of 44 to 55 mg/l to a level of 27 to 34 mg/l and at Ames, Iowa, from 18.6 to 10.4 mg/l. The floor space occupied by the Illinois unit is 45 sq ft per mgd capacity; that taken up by the Iowa unit is 86 sq ft per mgd. The area of the unit at Oklahoma State University is 38 sq ft per mgd. Flentje[16] reports that removals of carbon dioxide by cascade aerators vary from 20 to 45 per cent. Where climatic conditions make it necessary, these aerators can be housed to provide for winter operation.

3. *Multiple-tray Aerators.* Multiple-tray aerators consist of a series of trays equipped with slat, perforated, or wire-mesh bottoms over which water is distributed and caused to fall to a collection basin at the base. In most aerators coarse media such as coke, stone, or ceramic balls—ranging from 2 to 6 in. in diameter—are placed in the trays to increase efficiency. This type of aerator produces good turbulence and exposes a large water surface area to the atmosphere. The time of contact can be increased by the addition of more trays. Coarse media are especially efficient when used as a preparatory step in the removal of iron and manganese, because the media become coated with films which catalyze oxidizing reactions of the minerals to cause their precipitation.

Three to five trays are frequently used, with the spacing between them varying from 12 to 30 in. The area required for the trays appears to vary from 23 to 73 sq ft per mgd capacity, with most of them requiring less than 30 sq ft. Housing for this type of aerator is less expensive than for the spray and cascade types because of the smaller space requirements.

Information on a number of typical multiple-tray aerators is given in Table 2-2. The rate at which carbon dioxide is removed by these aerators can be approximated by this empirical formula:

$$C_n = C_0 10^{-Kn} \tag{6}$$

C_n is the concentration of carbon dioxide (mg/l) after passing through n trays (including the distribution pan); C_0 is the concentration of carbon dioxide (mg/l) as determined originally in the water in the distribution pan; K is a coefficient (apparently ranging from 0.12 to 0.16) which depends on the amount of ventilation and other characteristics of the unit.

The similarity of Eq. (6) to Eq. (2) should be noted. The former does not contain the quantity S which appears in Eq. (2), but since this is only about

TABLE 2-2 Typical Multiple-tray Aerators

Installation	Design capacity, mgd	Area of trays, sq ft	Type and size of media	No. of trays including distribution pan	Vertical distance between pans, in.	Housing	Space per unit of capacity, sq ft/mgd	Operating results		
								Flow, mgd	CO$_2$, mg/l	
									Raw	Aerated
Naples, Fla.[a]	1.1	81	2-in. coke	4	18	Outside	74	0.67	28	4
Wichita, Kans.[b]	48	986	2-in. coke	5	18	Inside	21	30	21	7.9
Owensboro, Ky.[c]	10	280	Coke	6	14	Outside	28	5.4	34	8
Columbia, Mo.[d]	3	160	None	5	18	[d]	53			
Marshall, Mo.[e]	2	80	None	6	18	Inside	40	1.03	28	10
Memphis, Tenn.:										
Allen Station[f]	30	896	3- to 6-in. coke	10	15½	Inside	30	10.5	96	3.2
Sheehan Station[f]	30	690	Coke	6	16	Inside	23	22.6	38	10

[a] Removal of hydrogen sulfide and carbon dioxide.

[b] Removal of carbon dioxide. Has forced draft ventilation at rate of 29,500 cfm.

[c] Removal of carbon dioxide.

[d] Removal of hydrogen sulfide. Outdoors with roof and screen sides.

[e] Removal of carbon dioxide. Has forced draft ventilation at rate of 2,000 cfm.

[f] Removal of carbon dioxide. Natural ventilation through open walls.

0.5 mg/l, its omission results in no significant decrease in accuracy of the expression for raw water containing more than approximately 10 mg/l of carbon dioxide. The value of K in Eq. (6) is equivalent to k (A/V) in Eq. (2), and n in Eq. (6) takes the place of t in Eq. (2).

Wells[17] reports 35 to 45 per cent removal of dissolved sulfides by multiple-tray aerators with slat bottoms in Duval County, Florida.

DIFFUSED-AIR AERATORS

For an equal expenditure of energy, a unit of the diffused-air type provides a longer aeration time than the waterfall type because the rising bubbles have a lower average velocity than the falling drops. From the standpoint of gas exchange, this is a distinct advantage in favor of the diffused-air type. Other factors, including turbulence, surface area–volume ratio, and surface film thickness, however, also influence aerator performance; the waterfall type has the advantage in these respects. Diffused-air aerators conserve the hydraulic head and are not subject to freezing. On the other hand, they frequently have higher initial costs and may require greater expenditures for maintenance than waterfall aerators. When making a choice between the two types for any specific installation, due consideration must be given to the factors relating to the efficiency of operation in addition to those concerned with the cost and adaptability.

Diffused-air units generally consist of rectangular concrete tanks in which perforated pipes, porous diffuser tubes or plates, or patented impingement devices are inserted near the bottom. Compressed air is injected through the system to produce fine bubbles which, on rising through the water, produce turbulence resulting in a continual change of exposed surface. Tanks are commonly 9 to 15 ft deep and 10 to 30 ft wide. Deeper tanks require higher air compression, which adds to the cost of operation without corresponding improvement in the efficiency, since the rising bubbles expand and tend to coalesce. Shallower depths reduce the time of contact of the bubbles with the water and the effectiveness of the process. Ratios of width to depth should not exceed 2:1 if effective mixing is to be obtained. The length of the tank is governed by the desired retention period, which usually varies from 10 to 30 min.

The air diffusers are generally placed along one side of the tank so as to impart a spiral flow to the water, thereby creating turbulence and assisting in gas transfer. If porous tubes or perforated pipes are used, they may be suspended at about one-half the depth of the tank to reduce compression heads. If porous plates are used, they are located on the bottom of the tank. The amount of air that is required depends upon the purpose of aeration, but generally ranges from 0.01 to 0.15 cu ft of air per gallon of water treated. Sufficient diffuser capacity must be provided to supply air at these rates without excessive loss. Lateral baffles are used in some cases to prevent short circuiting through the basin.

The blower pressure required depends upon the depth at which the diffusers are placed and friction loss through the air distribution system. Power requirements will vary from 0.5 to 2.0 kw per mgd capacity, with an average of about 1.0 kw.

When porous diffusers are used, incoming air should be filtered carefully through an electrostatic unit or a filter of metal wool, glass, or hair impregnated with oil in order to minimize clogging.

Diffused-air aerators require less space than spray aerators and more than tray aerators. As there is usually no difficulty, however, in operating these tanks during the winter, the need for housing is eliminated. The space for a tank 15 ft deep, providing a retention period of 10 min per mgd capacity, is 62 sq ft per mgd. Longer retention periods—required when the unit is used for mixing chemicals—will require proportionately more space. A list of typical installations is given in Table 2-3.

PATENTED TYPES

In addition to the general types of installations discussed there are a number of patented kinds which can be purchased from manufacturers. No attempt will be made here to describe these units. Information about them should be secured from the operating and design data provided by the manufacturers.

TABLE 2-3 Typical Diffused-air-type Aerators

Installation	Capacity, mgd	Period of aeration, min	Objective	Air requirement, cu ft/gal	Power requirement per mgd capacity, kw
Petersburg, Ind.*	1.0	30	Odor removal–mixing	0.10	1.46
Huntingburg, Ind.*	0.4	8.5	Odor removal	0.15	0.75
St. Paul, Minn.†	48	0.16	Odor removal–mixing	0.01	
Brownsville, Tex.*	4	14	Gas removal–mixing	0.07	0.48
Ft. Atkinson, Wis.*	0.75	18	Iron and odor removal	0.16	1.87
Kenosha, Wis.†	11.6	0.21	Odor removal	0.01	

*Data from Roe.[18]

†Activated carbon also used for odor removal.

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3

Coagulation and Flocculation

By JESSE M. COHEN and SIDNEY A. HANNAH

Production of potable water from a water supply contaminated by naturally introduced or man-made pollutants involves a series of unit processes. An important process is that of coagulation and flocculation, which is discussed in this chapter. Several broad aspects have been considered, such as history, the nature and physical chemistry of particles, the theories of coagulation-flocculation, the factors affecting coagulation, control of coagulation, and the coagulants currently available. Of course, the discussion could have been written in greater detail, but this would be impractical, since this chapter would necessarily expand into many volumes. For those desiring further elaboration, an extensive bibliography has been appended.

INTRODUCTION

Ancient literature and archaeological evidence record man's relentless search for "pure" water. In the earliest days of man's existence, water was taken as found. It might be pure and abundant, plentiful but muddy, scarce but good, or both scarce and bad. To get more or better water, ancient man either found other sources or, because of necessity, devised methods to improve the quality of the available water. Man's earliest standards of quality were few: freedom from gross turbidity, taste, and odor. While his criteria of purity have become more complex and certainly more quantitative, the principles, methods, and materials for purifying water have remained remarkably similar from the earliest recorded date of about 2000 B.C. down to the present time. But except for the developments of the last few decades, the history of "treatment" of water is largely a record of empiricism and a description of an art rather than of a science.

When, after many centuries, watertight household vessels became available, man observed that water could be more or less clarified by storage in containers or by filtration through porous receptacles or sand layers, leaving the objectionable sediment behind. After a lapse of many more centuries, he discovered that sedimentation could be aided by adding a precipitant or coagulant. This recognition that coagulation aided both sedimentation and filtration and the use of a great variety of organic and inorganic materials mark the beginning of the treatment of water. Moreover, for the first time, man was not constrained to accept the quality of water that nature provided but rather was able to modify it to meet his demands for increasingly higher standards of water quality.

History of Coagulation

Sanskrit medical lore and Egyptian inscriptions afford the earliest recorded knowledge of water treatment, dating back perhaps to 2000 B.C. In addition to heating or boiling and filtration other methods of purifying water included the use of a variety of mineral and vegetable substances, principally the seed of *Strychnos potatorum*.

With time other substances were found to be effective coagulants. The list includes an amazing variety of materials among which were certain nuts (e.g., almonds), beans, macerated laurel, pounded barley, and many others.

Alum, the coagulant most widely used today, also has an ancient background and was known to the early Egyptians of 2000 B.C. Its use, however, as a coagulant for water conditioning was first mentioned by Pliny (ca. 77 A.D.), who described the use of both lime (chalk of Rhodes) and alum (argilla of Italy) as useful for rendering bitter water potable. It is interesting to note that alum was an important item of trade in the world of the ancient Egyptians, well before its usefulness for water treatment was known. By the fifteenth century, the preparation of purified alum had reached manufacturing dimensions. In 1461 Pope Pius II attempted to create a monopoly on the production of alum, and within 2 or 3 years the papal manufacture of alum required the services of no fewer than 8,000 workmen.

During the Dark Ages, the art of water treatment, as with much other technology, seems not to have advanced but was revived during the 1600s by Sir Francis Bacon and others. By 1767, the common people of England were successfully treating muddy water by adding 2 to 3 grains of alum to a quart and allowing it to flocculate, after which the supernatant was filtered.

While coagulation as an aid to sedimentation and filtration of individual household and small industrial water supplies had been practiced from ancient times, its use in large industrial plants seems to have begun in the early part of the nineteenth century. The earliest use of coagulation for the treatment of municipal water supplies occurred at Bolton, England, in 1881. Alum at the rate of 1½ grains per imperial gallon was added at the intake. From 1885 onward, coagulation was widely used to precede rapid-sand filtration. Thus, coagulation and filtration, each used in a small way through the ages, were finally wedded.

Coagulation for the improvement of public water supplies might have been utilized earlier had it not been for the influence of ill-informed or prejudiced people whose word was respected, notably Arago of France in 1837 and the Massachusetts Board of Health in the 1880s, as well as medical men who frantically protested against both coagulation and rapid filtration during the late nineteenth and early twentieth centuries. The investigations on the use of alum for water treatment reported by D'Arcet in 1838 and by Jeunet in 1865 were influential in dispelling doubts about the effectiveness of coagulation.

In 1884 the first patent on coagulation was granted to Isaiah Smith Hyatt, who, following a suggestion of Col. L. H. Gardner, Superintendent of the New Orleans Water Company, described the use of perchloride of iron as a coagulant with his system of rapid-sand filtration in the treatment of a turbid water. When a year later the Sommerville & Raritan Water Company of New Jersey adopted Hyatt's coagulation-filtration system, the use of coagulation as an adjunct of rapid filtration had its inception as a full-scale method of treatment.

In 1885, Austin and Wilber of Rutgers University published the results of the first scientifically conducted American investigation of alum as a coagulant. After testing a large number of salts, the authors concluded that none offered the advantages of alum. In the years 1895 to 1897 at Louisville, Kentucky, George Warren Fuller and his associates conducted a series of important experiments on turbid Ohio River water in which a series of coagulants were tried: alum or basic sulfate of alumina, potash alum, and lime. Of these, alum was found most suitable. These experiments established coagulation as an adjunct to rapid-sand filtration. Its use rapidly became more common, so that by the turn of the century coagulation combined with rapid-sand filtration was in full swing in this country.

Notwithstanding the use of perchloride of iron by Isaiah Hyatt in his first use of coagulation, it was aluminum sulfate that dominated the field of coagulants in the early days. Nevertheless, iron, either as metal or as part of a salt, was widely employed as a coagulant at several water-treatment plants in the latter part of the nineteenth century. William B. Bull in 1898 first introduced the use of a combination of ferrous sulfate and lime, preparing his ferrous sulfate by burning sulfur and reacting the sulfurous acid with iron scrap in a procedure devised by William Jewell. In 1912, E. V. Bull reported the first use of chlorinated copperas (ferrous sulfate reacted with chlorine) and, though this material was not tried again until 1928, it was then found useful by Hedgepeth and Olsen in the coagulation of a highly colored water. This latter application served to focus attention on iron salts, several of which are in use today. While such iron salts as ferric chloride, chlorinated copperas, and ferric sulfate are used, the sulfate of alumina (alum) still is the most widely used coagulant.

Other metals capable of producing a hydrous oxide floc have been suggested as coagulants. Both sodium zincate and titanium salts have been studied but have proved to possess no advantage over alum and have remained laboratory curiosities with no practical use in water treatment.

Need for Coagulation

With relatively few exceptions, surface waters require some kind of treatment before distribution to the consumer. Contaminants resulting from land erosion, dissolution of minerals, and the decay of organic vegetation have always been present in widely varying proportions in streams and have required removal to make the water potable. The need for such treatment is ever increasing because of the additional pollution contributed by an expanding industrial complex and a burgeoning human population.

Natural waters, polluted either by man or by nature, are likely to contain dissolved inorganic and organic substances, biological forms such as bacteria and plankton, and suspended inorganic material. To remove these substances, the usual unit processes include plain sedimentation, removal by coagulation generally followed by filtration, and chemical precipitation used generally to remove dissolved minerals like hardness components and iron and manganese. Other processes such as adsorption, aeration, ion exchange, oxidation, and distillation are also important for the removal of dissolved substances.

Coagulation, generally followed by filtration, is by far the most widely used process to remove the substances producing turbidity in water. These substances normally producing turbidity consist largely of clay minerals and microscopic organisms and occur in widely varying sizes, ranging from those large enough to settle readily to those small enough to remain suspended for very long times.

Coarser components, such as sand and silt, can be removed from water by simple sedimentation. Finer particles, however, will not settle in any reasonable time and must be flocculated to produce the larger particles that are settleable. The long-term ability to remain suspended in water is basically a function of both size and specific gravity. The importance of size is illustrated in Table 3-1, which shows the relative settling times of spheres of different sizes. It can be seen that the settling rates of the colloidal and finely divided (approximately 0.001 to 1 micron) suspended matter are so slow that removing them from water by plain sedimentation in tanks having ordinary dimensions is impossible. The enormous increase of surface area for a given weight of solids as the particles become smaller and more numerous is an important property of colloids which is discussed later.

Substances producing color, as distinct from turbidity, consist either of colloidal metallic hydroxides, iron for example, or of organic compounds having a much smaller particle size. These substances, too, can be removed by coagulation, which serves to agglomerate the very small particles into sizes which are settleable or can be removed by filters.

The process of coagulation may also find use, although not always, in the softening of hard water with lime or lime and soda ash. Softening is more properly a precipitation process, and coagulation is used to obtain a more rapid and complete settling of the precipitated hardness components.

A turbidity limit of 0.1 unit and a color limit of 3 units have been recommended by the American Water Works Association Task Group 225M on water quality criteria for high-quality finished water. These limits are readily obtainable by properly performed coagulation and filtration.

TABLE 3-1 Effect of Decreasing Size of Spheres

Diam. of particle, mm	Order of size	Total surface area*	Time required to settle†
10	Gravel	0.487 sq in.	0.3 sec
1	Coarse sand	4.87 sq in.	3 sec
0.1	Fine sand	48.7 sq in.	38 sec
0.01	Silt	3.38 sq ft	33 min
0.001	Bacteria	33.8 sq ft	55 hr
0.0001	Colloidal particles	3.8 sq yd	230 days
0.00001	Colloidal particles	0.7 acre	6.3 yr
0.000001	Colloidal particles	7.0 acres	63 yr minimum

*Area for particles of indicated size produced from a particle 10 mm in diameter with a specific gravity of 2.65.

†Calculations based on sphere with a specific gravity of 2.65 to settle 1 ft.

SOURCE: S. T. Powell, "Water Conditioning for Industry," McGraw-Hill, New York, 1954.

It should be pointed out here that even a high-quality treated water that meets the recommendation of residual turbidity of 0.1 unit still contains enormous numbers of particles. These either represent uncoagulated primary clay particles or fragments of coagulant floc which have passed through the filters. For example, simple calculation will show that each liter of treated water will contain about 2×10^8 (200 million) particles of insoluble alum coagulant, assuming a suspended solids content of 0.1 mg/l and spheres 1 μ in diameter with a specific gravity of 1.01.

Experimental evidence confirms that these computations and assumptions are valid, at least in order of magnitude. A laboratory coagulation and filtration of a turbid water produced an effluent with a turbidity of 0.11 unit. Chemical analysis showed a residual aluminum content of 0.06 mg/l. A count of the particles in the size range of 0.59 to 1.0 μ using an electronic particle counter revealed that each liter of this treated water contained 3.4×10^8 (340 million) particles, an experimental value that is quite consistent with the computed number.

Nature of Matter in Water

Matter in water may be broadly classified according to its origin as inorganic mineral matter or organic carbonaceous material. Substances producing turbidity are often inorganic, while those causing taste, odor, and color are generally organic compounds. The particles producing turbidity may be further classified according to their size, which may range from molecular dimensions to 50 μ or larger. The fraction greater than 1 μ in diameter is generally referred to as silt and will settle out on standing. The smaller particles, which are classified as colloidal, will remain suspended for very long times. Most attention has therefore been directed toward use of coagulation for removal of colloidal material, although this process also removes the larger particles.

A distinguishing characteristic of particles of colloidal dimensions is the ratio of the surface area to mass. This property is clearly apparent from Table 3-1. In a large particle the ratio is low, and mass effects such as sedimentation under gravity predominate. For colloidal material where the ratio is very high, the properties associated with the surface of the particle, such as electric charges and ionogenic groups, become more important.

Colloids, in addition to their characteristics of size and high surface area, have been further classified as hydrophobic (water-hating) and hydrophilic (water-loving). The terms "lyophobic" and "lyophilic" are more generally used to cover dispersion media other than water. The distinction between the two classes of colloids is not fundamental, and a continuous series of substances exists with properties intermediate between the two extreme types. A distinguishing property of hydrophilic substances is their ability to react spontaneously with water to form colloidal suspensions which can be dehydrated to the original material and then redispersed repeatedly. This class of compounds includes substances such as starch, gums, and proteins. Dispersions of hydrophobic substances, on the other hand, are generally prepared by physical or chemical means. If such dispersions are dehydrated, they do not spontaneously redisperse in water. Clays and metal oxides are largely hydrophobic in nature. Because of these properties, lyophilic and lyophobic colloids are sometimes called "reversible" and "irreversible" colloids, respectively. The distinction between the two classes of compounds is important in coagulation because in hydrophilic systems the particles chemically react with the water in which they are dispersed and with metal coagulants. Purely hydrophobic systems do not react with the water phase, and coagulation is achieved by reactions that are largely physical rather than chemical.

MECHANISM OF COAGULATION

Definitions

It has already been pointed out that the settling velocities of finely divided and colloidal particles under gravity alone are so small that ordinary sedimentation is not practical. It is necessary, therefore, to use procedures which agglomerate the small particles into larger aggregates, which then have the settling velocities required to be practical. Formation of larger particles from smaller ones is also required for their removal by filtration.

Historically, the terms "coagulation" and "flocculation" have been used indiscriminately to describe the process of removal of turbidity from water. There is, however, a clear distinction between the two terms.

The term "coagulation" comes from the Latin *coagulare,* meaning to drive together. This process describes the effect produced by the addition of a chemical to a colloidal dispersion resulting in particle destabilization by a reduction of the forces tending to keep the particles apart.

Operationally, coagulation is achieved by adding the appropriate chemical which causes particles to stick together when contact is made. Rapid mixing is important at this stage to obtain uniform dispersion of the chemical and to increase the opportunity for particle-to-particle contact. The entire process occurs in a very short time, probably less than a second, and initially results in particles submicroscopic in size.

The second stage of the formation of settleable particles from destabilized colloidal-sized particles is termed "flocculation." This term also has its derivation from the Latin, in this case *flocculare*, meaning to form a floc, which visually resembles a tuft of wool or highly fibrous porous structure. In contrast to coagulation, where the primary force is electrostatic or interionic, flocculation occurs by a chemical bridging or physical enmeshment mechanism. Flocculation is operationally obtained by gentle and prolonged mixing which converts the submicroscopic coagulated particles into discrete, visible, suspended particles. At this stage, the particles are large enough to settle rapidly under the influence of gravity and may be removed from suspension by filtration.

The more usual practice has been to physically separate the unit processes into coagulation-flocculation, sedimentation, and filtration. There have been recent efforts to condense these processes by reducing flocculation time and shortening or even eliminating the sedimentation basin, thus relying on the filters for part of the flocculation process.

Stability and Instability Factors

At this point, it is necessary to consider the factors which cause particles to remain in suspension as well as those which result in coagulation. These conditions are described by the terms "stability" and "instability" of colloidal suspensions. Stability refers to the inherent property of colloidal particles to remain dispersed despite passage of time, whereas instability describes the tendency of particles to coalesce whenever particle-to-particle contact is made. Historically, two broad theories have been proposed to explain the mechanisms involved. The older (chemical) theory assumes that colloids acquire electrical charges on their surfaces by ionization of chemical groups present at the surface and that coagulation or destabilization is accomplished by chemical interactions between colloid particles and coagulant. The physical theory, on the other hand, emphasizes such physical factors as electrical double layer and counterion adsorption where destabilization occurs through reduction of forces such as zeta potential. Each theory has had its time of ascendance of popularity, but it now appears that the mechanisms are not mutually exclusive, and both theories have to be invoked to explain the process of coagulation in water-plant systems where a heterogeneous mixture of colloid systems exists.

Stability Forces

Since the objective of coagulation is to destabilize particles to permit formation of aggregates, it is important to consider here the forces which cause stable suspensions. For hydrophilic colloid systems, stability is maintained by the phenomenon of hydration, in which water molecules are attracted to the surface of the particles and act as a barrier to contact between particles.

It is now generally agreed among colloid scientists that stability of hydrophobic particles is due largely to the phenomenon of the electrical double layer consisting of the charged-particle surface and a surrounding sheath of ions of charge opposite to that of the particle surface. Several theories have been advanced to quantitatively describe the concept of the electrical double layer. The theory was first proposed by Helmholtz in 1879 and subsequently modified by a number of workers, among them Gouy, Chapman, and Stern, with the latter's theory being more generally accepted. These theories are too complex to be discussed here in detail. In its simplest form, the theory states that hydrophobic particles suspended in water carry electrical charges at their surfaces. For particles in natural waters, the charge is usually negative. These electrical charges may arise through ionization of atoms at the particle surface, by replacement of elements in a crystal lattice by elements having a different charge, or particles may acquire the charge through adsorption of ions, particularly hydroxide ions, from the water itself. These ions are tightly bound to the surface of the particle and attract ions of opposite charge from the mixture of positive and negative ions in the water. This layer of oppositely charged ions (called "counterions") is held near the particle by the electrostatic forces. Thermal agitation of the molecules of water causes the counterions to form a diffuse layer extending out from the particle surface into the bulk solution. As shown in Fig. 1 the potential decays exponentially from the particle surface and eventually becomes zero where equal concentrations of cations and anions are present.

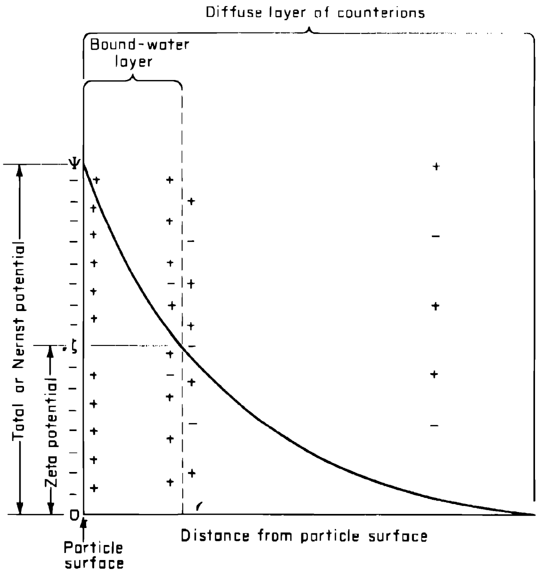

Diffuse layer of counterions
Bound-water layer
Ψ
ζ
0
Total or Nernst potential
Zeta potential
Distance from particle surface
Particle surface

Fig. 1 Structure of a double layer and the corresponding potentials. Ψ is at the particle surface, and ζ is at the hydrodynamic plane of shear.

It is no longer possible, therefore, to consider particles in water as discrete portions of matter suspended or moving in a liquid. Rather, each particle is a complicated entity consisting of several components in addition to the primary particle. Several distinct layers can be described. These are schematically illustrated in Fig. 1. The particle surface is shown as a plane containing negatively charged ions. Cations from the bulk solution are attracted to this surface. At increasing distances from the particle, the forces of attraction quickly decrease, and there arises a diffuse layer of ions trailing out into the bulk solution. At some distance from the particle and within the diffuse layer there is a plane of shear representing the portion of bound water and ions that will remain attached to the particle as it moves through the suspending liquid. Hence, in a sense, the bound-water layer can be considered as an integral part of the charged-particle surface. It is important to note here that the thickness of the double layer relative to particle diameter is extremely small. The distances shown in the figure have been exaggerated for illustrative purposes. For example, the thickness of the double layer in a solution of monovalent ions at a concentration of 10^{-3} molar (about the concentration in surface water) is approximately 100 Å (0.01 μ).

A consequence of the electrical double layer surrounding each particle in water is to create regions of electrical potential in a bulk solution that nominally has a zero potential. The electrostatic work required to transport a unit charge from this bulk solution through the phase boundaries of each layer surrounding a particle to any point measures the potential at that point. The potential increases sharply with increasing approach to the primary particle surface. The potential at the surface of the particle, also called the "total potential" or Nernst potential, is represented by Ψ (psi). For certain surfaces of known composition, Ψ can be calculated. However, its value is unobtainable for impure colloids of interest in water treatment.

The second potential of interest is called the "zeta potential" (ζ), and is located at the "plane of shear," that is, at the boundary between the solvent adhering to the particle in its motion and that which can move with respect to it. This "plane of shear" essentially separates the water of hydration from free water.

The zeta potential is interesting and important because it is related to particle stability, and approximate values of zeta potentials can be calculated from easily measured electrophoretic mobilities. It should be pointed out, however, that the zeta potential does not measure the total potential, but rather a portion of it.

The net effect of the existence of electrical double layers around particles is to inhibit the close approach of particles to each other, and hence the double layers confer stability to the suspension. Both the thickness of the double layer and the surface-charge density are sensitive to concentration and valence of the ions in solution, and hence stability of the suspension can be markedly affected by adding suitable ions to the solution.

Instability Forces

While the phenomena of surface hydration and double-layer formation contribute to the stability of colloidal particles, there are forces which operate in the opposite direction to cause the particles to become destabilized or coagulated.

One of the factors generally cited as important to instability of colloid particles is Brownian movement. Very early in the study of colloidal systems it was discovered that very small particles suspended in water, particularly those with particle diameters 100 mμ or less, are in constant motion. The energy for this motion of the particles is obtained from collisions with water molecules and is directly related to temperature, the energy increasing with increasing temperature. The particles are bombarded from all directions, resulting in a rapid and random movement of the colloids. While this translocation of particles contributes to instability of the colloidal suspension in that the probability of particle collisions is increased, these contacts will not, however, result in a sufficient number of lasting unions unless the colloids have already been destabilized. Moreover, for larger particles, Brownian movement becomes a negligible factor. A far more effective way of promoting particle collisions is to establish hydraulic gradients by mixing or by creating areas of turbulence.

Another force which is always a force of attraction between particles and leads ultimately to instability is the London–Van der Waals force. It may be described as an atomic cohesive force and exists between all atoms. In any assembly of atoms, each atom attracts every other atom. Although these forces are generally considered to operate within distances of the order of atomic dimensions, in the case of colloidal particles the aggregate effect of the attractive forces is to extend the range of effectiveness to the order of colloidal dimensions.

If the electrical forces of repulsion between particles are sufficiently reduced to permit particle-to-particle contact, then the London–Van der Waals forces will cause particles to stick to each other, leading to progressive agglomeration of particles.

Because an approximate value for the zeta potential of particles can be readily determined by a variety of methods, generally by electrophoretic mobility measurements, numerous attempts have been made to correlate zeta potential with coagulation. Experimental evidence generally leads to the conclusion that coagulation of colloids in water is often obtained well before complete reduction of the zeta potential to zero, the value generally ranging from —5 to —10 mv or less. This lack of exact correlation of zeta potential and coagulation can be explained on a theoretical basis. As indicated in Fig. 1, the zeta potential denotes the potential at the "plane of shear" between the particle complex and the bulk solution; but the forces of attraction extend appreciably beyond this point, so that a measurement of zeta potential cannot be a completely reliable indication of stability. In practice, however, an empirical relationship can often be established between zeta potential and instability or coagulation, and this experimentally derived value then becomes useful to control a coagulation under those specific conditions. The optimum zeta potential value is usually negative with the usual systems in water.

Summary of Forces

The forces described above, some or all of which may be operating in any colloidal system, can be summarized as follows:

The forces that tend to keep particles apart and hence lead to stable colloidal suspension are hydration, which results in a protective shell of water molecules, and electrical double layer, which produces electrical potentials that act as barriers to the close approach of other particles.

Instability of suspensions (coagulation) is the result of particle-to-particle contact; the kinetic energy for particle translocation is obtained from Brownian movement for the smaller particles, but more importantly from the energy introduced into a colloidal suspension in the form of mixing or turbulence which greatly increases the probability of particle collisions if the forces of repulsion are sufficiently reduced and if the hydration layer is thin enough. After particle contact is made, Van der Waals forces will cause the particles to stick to each other, resulting in progressive agglomeration of particles.

THEORY OF COAGULATION

Up to this point, the purely internal forces have been described. Some or all of these forces operate in any colloidal suspension. It is apparent, however, that additional but external forces can be added to the colloidal system to either promote or decrease the stability of the system. In water treatment the objective is to destabilize and to increase the particle size of the colloids.

Classical Colloid Chemistry

During the 1800s, the classical colloid chemists working with monodisperse colloidal sols at relatively high concentrations observed that coagulation could be obtained by addition of electrolytes. Schultze in 1882 and Hardy in 1900 studied these reactions quantitatively, and the results of their studies led to what are now known as the Schultze-Hardy rules.

Essentially, they stated that coagulation is caused by ions having a charge opposite to that of the colloidal particles and that the coagulating power of an ion is markedly dependent on its valency. Thus, a bivalent ion is approximately 30 to 60 times more effective than a monovalent ion, and a trivalent ion is 700 to 1,000 times more effective than a monovalent ion. They further showed that the stability of a colloidal suspension was due to the electrical repulsion existing between particles and that the introduction of ions of opposite charge results in charge neutralization with consequent zeta potential reduction to zero. Under these conditions coagulation of the colloid occurs.

It was shown by others that coagulation of a colloid could also be achieved by colloids of opposite charge as well as by ions. This reaction was termed "mutual coagulation."

Derjaquin and Verwey in 1940 and 1941 and Overbeek in 1948 placed the above reactions on a quantitative basis. Their theoretical calculations essentially confirmed the Schultze-Hardy rule of valency dependence. They also showed that stability was not due to the electrical repulsion between two primary particles but that this reaction had to consider the interaction between two particles, each of which was surrounded by an electrical double layer. The effect of the double layer was to prevent the close approach of particles to distances within which the short-range London–Van der Waals forces could operate to cause coagulation. The net effect, however, of the addition of electrolytes is to decrease the thickness of the electrical double layer and at certain concentrations, depending on the ion involved and particularly on its valency, coagulation would occur because of the reduction of the barrier to close approach of particles.

An important point that emerges from their work is that zeta potential is not a determining measure of this reduction of double-layer interaction and consequent increase in extent of coagulation. More important than zeta potential is the reduction in double-layer thickness. While zeta potential tends to approach zero, coagulation is possible well before electrical neutrality is achieved.

In considering coagulation, whether by electrolytes or by colloid interaction, the element of time is important. The simplest case of coagulation occurs when enough electrolyte has been added to so reduce the double-layer barrier that each contact between particles as the result of Brownian movement produces an irreversible coalescence. Smoluchowski has shown that under these conditions coagulation is rapid.

Under conditions where only enough electrolyte has been added to partially reduce the thickness of the double layer, then coagulation is slow. It has also been shown that rate of coagulation is determined by particle size, shape, and heterogeneity.

Practical Colloid Chemistry

While the theories of coagulation just described have proved to be useful tools for the classical colloid chemists, the application to coagulation in water treatment has been much less successful, principally because of the differences in the colloid systems. In water treatment colloids are not single species but rather are a heterogeneous mixture of particles with widely varying size, shape, and chemical composition; colloids and electrolytes are present in very low concentrations; and finally, coagulation in water treatment is invariably obtained by using salts which hydrolyze in water, and the interactions between colloid particles on the one hand and colloids resulting from the hydrolysis of metal salts on the other hand have posed problems which colloid chemists have not yet been able to resolve fully.

COAGULATION IN WATER TREATMENT

Although the coagulation process using aluminum and iron salts as coagulants is ancient and has been in continuous use for the past 100 years to the present, knowledge of the precise mechanism has generally been lacking. In its empirical form, the process is deceptively simple; alum or iron salt is added to turbid water to form a flocculent material that can be settled or filtered out, and the result is clarified water. The original conception of the mechanism postulated that immediately upon addition of aluminum or iron salts to water containing turbidity, ionization produced tripositive aluminum or ferric ions. Then borrowing from the classical colloid chemical theory, the hypothesis assumed that the positively charged coagulant ions neutralized the negatively charged turbidity particles, removing the forces of mutual repulsion existing between the particles, and agglomeration resulted.

Even though Mattson, as early as 1929, had pointed out that the hydrolysis products of aluminum and ferric salts were more effective in coagulation than the ions themselves, his work was largely ignored by the water-treatment field. Theories of coagulation based on the tripositive metal ions continued to be expressed as late as the early 1960s.

It is now known that the earlier-held views were incorrect, and that the products of hydrolysis of aluminum and iron, and not the metal ions themselves, must be considered as the coagulating agents. It had also been previously held that the presence of nuclei around which the floc could form was essential in water, and this view, too, has been shown to be erroneous.

Chemistry of Metal Coagulants

It has long been known that, when added to water, aluminum and iron salts will react with the water or with alkalinity present in the water. This reaction was thought to yield the insoluble material aluminum or ferric hydroxide, represented as $Al(OH)_3$ or $Fe(OH)_3$. In the reaction an acid was produced which reduced the pH of the solution and consumed alkalinity in approximately the ratio of 1 mg/l of alkalinity for each 2 mg/l of commercial filter alum. Discrepancies in this ratio and the fact that the aluminum hydroxide floc frequently contained ions other than aluminum and hydroxyl ions, notably sulfate, suggested that the reaction was not, in fact, as simple as represented. Indeed, the hydrolytic chemistry of aluminum and iron is exceedingly complex.

Hydrolysis of Aluminum Salts

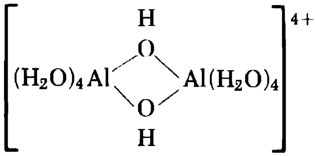
When an aluminum salt is added to water, a series of reactions occurs with the water itself (or with other ions in the usual natural waters), a process broadly described as hydrolysis. The currently held view, supported by theoretical and experimental evidence, is that aluminum ions, almost instantly after addition to water, enter into a series of hydrolytic reactions with water to form a series of multivalent charged hydrous oxide species. Depending on pH, these compounds may range from positive at the lower pH values to negative at the more basic pH values. These reactions can be represented as follows:

$$[Al(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Al(H_2O)_5OH]^{2+} + H_3O^+$$

$$[Al(H_2O)_5OH]^{2+} + H_2O \rightleftharpoons [Al(H_2O)_4(OH)_2]^+ + H_3O^+$$

This reaction can proceed until the neutral species $[Al(H_2O)_3(OH)_3]$ or a negatively charged species $[Al(H_2O)_2(OH)_4]^-$ are formed.

Recent evidence suggests, however, that the monomeric species, i.e., those compounds containing only one aluminum ion, are at best transient, and that a second type of reaction called "olation" is the more important in coagulation. In the process of olation, a series of polymerization reactions occurs, resulting in complexes containing several aluminum ions bridged by two hydroxyl groups. A model of a simple complex containing two aluminum ions can be illustrated as follows:



It has been suggested that the complex most important in coagulation at low concentrations of aluminum is a polynuclear complex containing eight aluminum ions carrying a tetrapositive charge, of the form

$$[Al_8(OH)_{20}]^{4+}$$

One of the significant points that emerge from the study of these reactions is that both hydroxide and hydrogen ions are involved; thus pH plays an important role in coagulation. The pH of the water is of primary importance in establishing the average charge of the hydrolysis products and consequently is significant in determining the rate of coagulation. In addition to pH, the chemical composition of water also influences the species of complex produced, since negative ions other than hydroxide, particularly the di- and trivalent ions, may enter the complex and significantly change its properties. Thus in the presence of, for example, sulfate, one or more sulfate ions may substitute for hydroxide ions in the manner shown below:

$$[Al(H_2O)_6]^{3+} + SO_4^{2-} \rightleftharpoons [Al(H_2O)_4SO_4]^{+} + 2H_2O$$

In this case the divalent sulfate ion has substituted for two hydroxide ions yielding a monopositive aluminum complex.

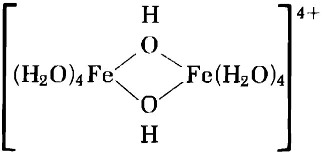
The practical significance of the effects of ions on coagulation will be discussed later.

Hydrolysis of Iron Salts

The hydrolysis of iron is similar to that of aluminum. Thus iron undergoes a series of hydrolytic and olation reactions with the formation of ferric hydroxo and polynuclear complexes. The hydrolytic type of reaction yields the following:

$$[Fe(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Fe(H_2O)_5OH]^{2+} + H_3O^{+}$$

Iron has a greater tendency than aluminum to polymerize through the olation reaction to form metal hydroxo polymers of the type



Mechanism of Floc Formation

With the foregoing brief description of the physical and chemical behavior of the colloids initially present in turbid water and of the colloids formed from the external addition of aluminum or iron salts, it is now possible to depict the series of events that can occur.

Turbid water contains, in addition to dissolved and settleable solids, colloids which are electrically charged. The charges induce the formation of electrical double layers, and stability of the colloidal system is established by the forces of repulsion existing in the interaction between double layers.

Immediately upon addition of aluminum or iron salts to the water, reactions with water and other ions occur, resulting in the production of multipositive hydroxo and polynuclear species of compounds. The coagulant species are rapidly adsorbed onto the surface of the turbidity particles, which ultimately become "coated" with coagulant. The electrostatic attraction between the negatively charged particles and the positively charged hydrolysis products enhances the deposition. The net result is that the electrical charges on the particle are reduced. Depending on pH and coagulant dose, the charge on the particle as measured by zeta potential may vary from slightly negative to neutral to slightly positive. The suspension is now considered to be destabilized and the process of flocculation, where the particles can agglomerate to settleable size, can proceed unhindered. Mixing or turbulence promotes collisions, and because the particles have now been destabilized, each collision results in a lasting union.

In addition to the above process, which is dependent on electrostatic forces for adsorption and attraction, a purely physical or mechanical process may be taking place concurrently. Under the proper conditions for the coagulation, and even in the absence of turbidity, coagulants will hydrolyze and form progressively larger masses of flocculent material. In the process of this formation and during its settling when sufficient size has been attained, the floc may also physically enmesh the turbidity particles and simply act like a "sweep" as it settles. It is not known what relative importance the two mechanisms, electrostatic and enmeshment, have in any coagulation-flocculation system, but undoubtedly both play a role.

In contrast to the mechanisms just described for the coagulation of hydrophobic particles (generally clay turbidity), a slightly modified mechanism must be considered for the destabilization of hydrophilic colloids, of which an important example is natural color in water. A characteristic of hydrophilic colloids is that they contain polar groups such as hydroxyl, carboxyl, or phosphate groups that are negatively charged. They are thus able to combine chemically, rather than by electrostatics, with the positively charged coagulant hydrolysis products, forming an insoluble product that is electrically neutral or destabilized. The process of flocculation to settleable size can then proceed as described above for hydrophobic colloids.

FACTORS INFLUENCING COAGULATION

Optimum coagulation treatment of a raw water represents the attainment of a very complex equilibrium in which many variables are involved. Thus, for a given water, there will be interrelated optima of conditions such as pH, turbidity, chemical composition of the water, type of coagulant, and such physical factors as temperature and mixing conditions. These interrelations are so complex that at the present time it is impossible to predict from purely theoretical bases the optimum coagulant dose for any particular water. The proper dose and physical conditions for coagulation must be determined empirically for each water by methods that will be discussed later. Notwithstanding these difficulties, a knowledge of the effects on coagulation of the several variables can lead to a more intelligent application of empirical methods.

Effect of pH

Early investigators of the coagulation process in water treatment showed that pH was the single most important variable of the many that had to be considered. These investigators clearly established that there is at least one pH range for any given water within which good coagulation-flocculation occurs in the shortest time with a given coagulant dose. The extent of the pH range is affected by the type of coagulant used and by the chemical composition of the water as well as by the concentration of coagulant. Whenever possible, coagulation should be carried out within the optimum pH zone. Failure to operate within the optimum zone for a given water may be wasteful of chemicals and may be reflected in lowered quality of the water-plant effluent.

The metal coagulants, aluminum and iron salts, have been shown to precipitate and coagulate most rapidly and with minimum solubility in some characteristic pH range, depending on the particular coagulant. Extensive and continuing investigations beginning in the early 1920s and extending to the present have shown that the pH zone of least solubility for the hydrolysis products of aluminum ranges from 5.5 to 7.8. In practice, in the presence of ions and turbidity normally present in natural waters, the pH range is generally 6.0 to 7.8. Iron salts behave similarly, although the pH zone of coagulation is generally broader.

Interrelations between pH and required alum dosage to coagulate clay, residual aluminum, and turbidity of precipitated coagulant are shown in Fig. 2. Curve *A* shows that the minimum dose to remove 50 mg/l clay turbidity occurs within a pH range of 6.8 to 7.8; residual aluminum after treatment with 200 mg/l of alum, shown in curve *B*, is minimal at a pH of between 5.5 and 7.5; and flocculation of aluminum hydroxide in the absence of clay, shown in curve *C*, occurs most rapidly at a pH of about 7.2. The data represented in the curves shown in Fig. 2 have been cited as evidence that aluminum sulfate is most efficient as a coagulant of dilute clay suspensions under conditions which produce the most rapid precipitation and flocculation of its hydrolysis products. Thus, experimental data corroborate the theoretical concept that the coagulating agent is hydrolysis products and not trivalent aluminum ion. Curve *C*, representing coagu-

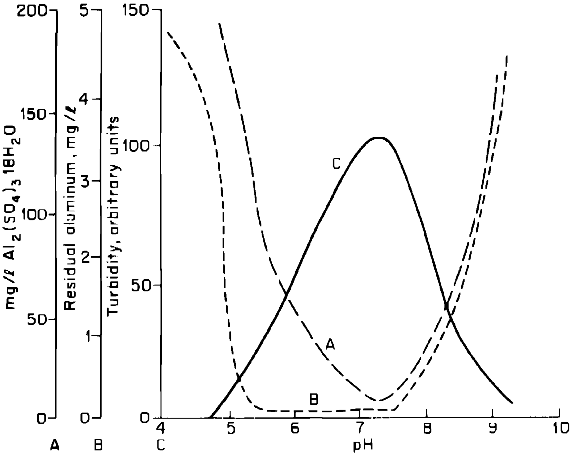


Fig. 2 Comparison of the effect of pH on: Curve *A*, dose of aluminum sulfate required to halve turbidity of 50 mg/l clay suspension; curve *B*, aluminum solubility as indicated by residual aluminum after coagulation with 200 mg/l $Al_2(SO_4)_3 \cdot 18\ H_2O$; curve *C*, flocculation of $Al(OH)_3$ as indicated by the turbidity 1 min after mixing the reagents. [*Adapted from R. F. Packham, Proc. Soc. Water Treat. Exam.*, 12:*15 (1963).*]

lation with no clay turbidity present, also demonstrates that coagulation and flocculation of alum alone will occur with no dependence on turbidity to serve as either nuclei or electrical charge sites.

Coagulation should, if possible, be carried out within the optimum pH zone for the particular water. For certain waters it may be necessary to adjust the pH with acid, lime, soda ash, etc., to obtain the proper conditions. Addition of excess coagulant may in some plants be a more practical way to reduce pH to the favorable range than separate acid addition. With optimum pH conditions, the soluble residual aluminum concentration in the effluent will be exceedingly small; however, under practical conditions of coagulation, colloidal insoluble particles of aluminum hydroxide may appear in the effluent in concentrations ranging from 0.01 to about 0.1 mg/l of aluminum. Concentrations of aluminum much higher than the upper value would indicate incomplete flocculation or penetration of alum floc through the filters.

Effect of Salts

Natural waters are never pure water but are dilute solutions of inorganic salts of varying concentration and composition. The effects of these salts on the coagulation process have been extensively studied and have been shown to exert an influence, depending on the specific ion and its concentration. The principal effects of the presence of certain ions are to alter (1) the pH range of optimum coagulation, (2) the time for flocculation,

(3) the optimum coagulant dose, and (4) the residual coagulant in the effluent. Some of these effects can be partially explained on the basis that certain inorganic ions can substitute for hydroxide ions in the aluminum hydroxide complexes. This can account, at least qualitatively, for the greater influence anions have compared to cations and for the increased influence of di- and trivalent anions compared to the monovalent anions. A consequence of the substitution of a different anion for a hydroxide ion is to produce a compound with a different solubility.

Black, Rice, and Bartow in 1933 investigated the effects of varying salts on the coagulation and flocculation of alum by measuring the rate of floc formation. The effect of the sulfate ion SO_4^{2-} on alum coagulation is shown in Fig. 3. In the absence of additional sulfate ions the pH zone of

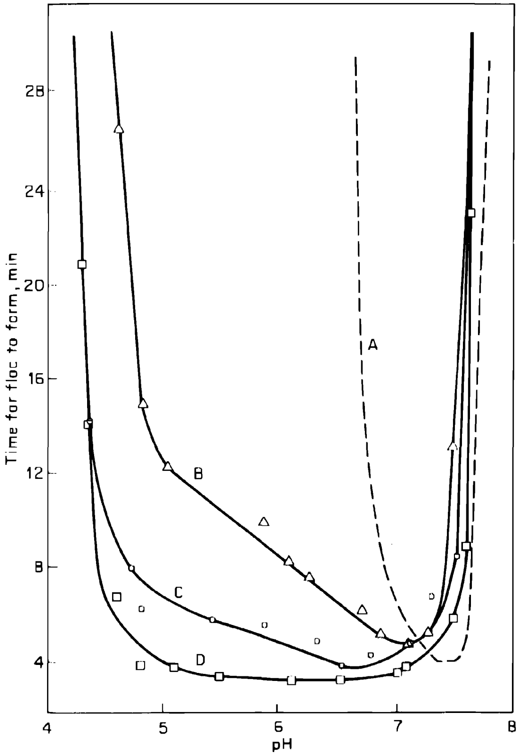


Fig. 3 Effect of sulfate ion on time of formation of alum floc. Broadening of the pH zone of coagulation by sulfate ion. Curve *A*, alum, 35 mg/l, and sodium hydroxide; curve *B*, addition of 25 mg/l SO_4; curve *C*, addition of 50 mg/l SO_4; and curve *D*, addition of 125 mg/l SO_4. [*After A. P. Black, Owen Rice, and Edward Bartow, Ind. Eng. Chem.*, 25:*812 (1933)*.]

floc formation is narrow with a minimum in the curve occurring at a pH of about 7.5. As the sulfate ion is increased, the pH zone is markedly broadened extending toward the acid side. With 125 mg/l of additional sulfate ion, floc formation is obtained within a broad pH zone extending from 4.8 to 7.2.

A somewhat different effect is produced by the phosphates. In this case, as shown in Fig. 4, the minimum dose of alum required to remove one-half of the turbidity is shifted toward the acid side with little or no broadening of the pH range as occurred with the sulfate ion. In the absence of phosphate ions the minimum in the curve occurs at a pH of about 7.2. As the phosphate concentration increases, the minimum is shifted toward the acid side until, with 158 mg/l, the minimum occurs at a pH of about 5.0.

Extensive experimentation such as the foregoing has led to the following generalizations on the effects of ions on coagulation:

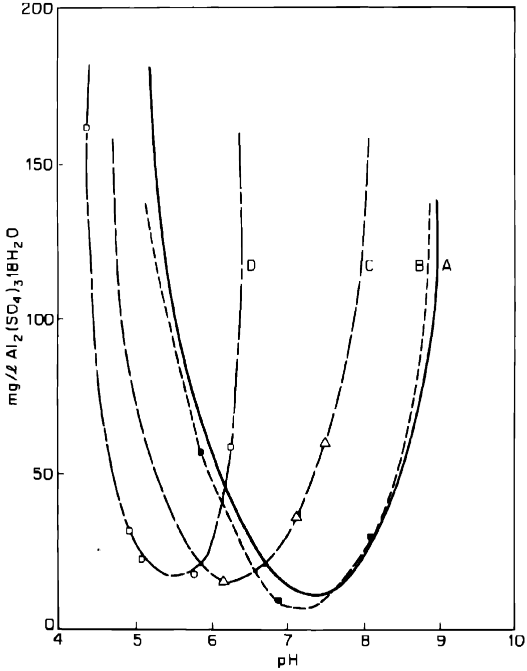


Fig. 4 Effect of orthophosphate on pH zone of coagulation. Points on the curves represent the alum dosage required to reduce 50 mg/l of clay turbidity to one-half its original value. Curve *A*, alum alone, no PO_4; curve *B*, 4.8 mg/l of PO_4 added; curve C, 48 mg/l of PO_4 added; and curve *D*, 475 mg/l of PO_4 added. Presence of orthophosphate displaces the pH zone of coagulation toward the acid side. [*After R. F. Packham, Proc. Soc. Water Treat. Exam.*, **12:** *15 (1963).*]

1. In general, coagulation with aluminum or iron salts is subject to greater interference from anions than from cations. Thus, ions such as sodium, calcium, and magnesium have relatively little effect on coagulation.

2. Anions extend the optimum pH range for coagulation to the acid side to an extent dependent on their valency. Thus monovalent anions such as chloride and nitrate have relatively little effect, while sulfate and phosphate cause marked shifts in pH optima.

While the above effects can readily be demonstrated in the laboratory, the application of this knowledge in practical coagulation of natural waters is difficult. Natural waters contain a complex mixture of ions, and it simply is not possible to separate the effects of the individual ions from the net effect of all ions. The proper dose of coagulant and the optimum pH must be determined for each water, but knowledge of the effects of ions can lead to a more informed approach to the determination.

Effect of Nature of Turbidity

The nature of the turbidity must also be considered. As described earlier, turbidity in surface waters consists largely of clay and other mineral particles. The size range of most of these particles is about 0.2 to 5.0 μ, which places them in the upper size range of true colloids and in a size range which would settle under gravity if given sufficient time. Coagulation of such suspensions is accomplished relatively easily, once the proper pH has been determined. The following generalizations can be made:

1. A certain minimum of coagulant must be added for any clay turbidity concentration in order to provide an enmeshing mass of floc.

2. Some additional coagulant is generally required with increase in turbidity, but the dosage of coagulant will not increase linearly with increase in turbidity.

3. Paradoxically, with very high turbidities relatively smaller coagulant doses are required because of the high collision probabilities; for the same reason the very low turbidities are frequently more difficult to coagulate.

4. The exchange capacity (the quantitative expression of the ability of clays to exchange cations, i.e., calcium for sodium, etc.) of the turbidity in water does not seem to be important, although it has been suggested that increasing exchange capacity was the cause for increasing coagulant demand.

5. The organic matter frequently adsorbed on clays from natural stream waters does not increase coagulant demand.

6. A broad distribution of clay particle sizes is much easier to coagulate than a suspension containing a single or narrow range of particle sizes.

In general, coagulation of dilute clay suspensions is controlled more by the coagulant and the chemical composition of the water than by the nature of the suspended solids.

Waters containing organic colloids derived from pollution by sewage and industrial wastes are invariably more difficult to coagulate, and coagulant doses can rise because of the extensive chemical reactions that occur between the coagulant and the colloidal organic matter.

Effect of Coagulant

One of the factors influencing coagulation that is within the control of the water plant operator is the choice of coagulant. While alum is by far the most commonly used coagulant, iron salts can be used as well and in some instances have advantages over alum. A significant advantage of iron salts over aluminum is the broader pH range for good coagulation. Thus, in the treatment of soft colored waters where color removal is best obtained at acid pH's, the use of iron salts is preferable. The greater insolubility of ferric hydroxide at alkaline pH's, in contrast to aluminum salts which form soluble aluminate ions at basic pH's, suggests that iron salts should be considered under these conditions. Sodium aluminate is, however, used for coagulation of softening precipitates at high pH.

The considerable differences in pH zones of good coagulation between aluminum and iron salts are illustrated in Fig. 5. For alum the pH zone for optimum coagulation is quite narrow, ranging from about 6.8 to 7.5; the comparable range for ferric sulfate is considerably broadened, to a pH range of about 5.5 to 8.8.

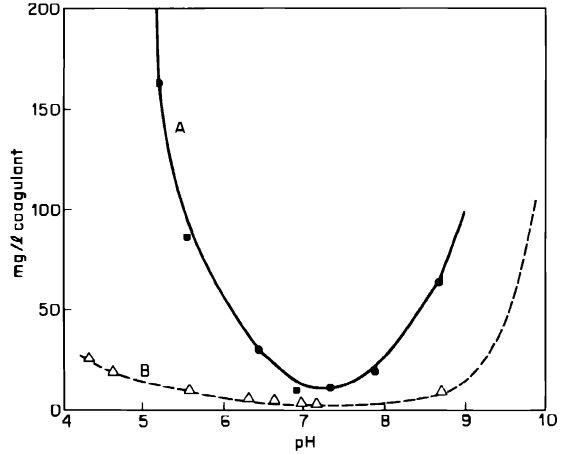


Fig. 5 Coagulation of 50 mg/l kaolin with aluminum sulfate and ferric sulfate. Comparison of pH zones of coagulation of clay turbidity by aluminum sulfate, curve *A*, and ferric sulfate, curve *B*. Points on the curves represent the coagulant dosage required to reduce clay turbidity to one-half its original value. [*Adapted from R. F. Packham, Proc. Soc. Water Treat. Exam.*, 12: *15 (1963).*]

The choice of the coagulant to be used for any particular water should be based on an experimental comparison of performance, with the final choice being influenced by economics.

Effect of Physical Factors

Little experimental information is available on the effect of temperature on coagulation, particularly the effect of temperatures near freezing, although water plant operators generally agree that difficulties are encountered during periods when water temperatures approach 0 °C. The settling characteristics of the floc become poor, and there is an increased tendency of floc to penetrate the filters, suggesting that floc strength has decreased. The specific reasons for these difficulties are not known, although certain changes occur with decrease in temperature.

As temperature decreases, the viscosity of water increases, and hence the rate of settling of floc is decreased. While decrease of temperature is known to decrease the rate of chemical reactions, this effect on coagulation is probably too small to be significant. It has been observed, however, that the optimum pH value is decreased by decreases in temperature and that this shift becomes more important with smaller doses of coagulant.

The difficulties arising from cold temperatures can generally be overcome by (1) conducting the coagulation as near as possible to the pH optimum for that water at that temperature, (2) increasing the coagulant dose, which not only increases collision probabilities of particles but reduces the effect of optimum pH shift, or (3) adding aids in the form of clays to increase floc density and coagulant aids such as activated silica and polyelectrolytes to increase floc strength and promote more rapid settling.

Presence of Nuclei

It was once thought that nuclei or particles were essential for coagulation or the initial formatiom of floc, although it is currently agreed that hydrolysis and subsequent precipitation of coagulants can be obtained in the complete absence of solid suspended particles. Particles, particularly as the numbers increase, do influence the rate of flocculation and contribute to increased density of floc and hence increased settling velocities. The small numbers of particles characteristic of low-turbidity waters contribute to the low rate of floc formation and the poor settling characteristics of the floc.

These difficulties are sometimes remedied by returning part of the settled sludge from previously treated water to the incoming water. This principle of returning preformed floc to water is sometimes utilized in mechanical flocculation. In this system, the first floc that settles is picked up and returned to the basin where fresh coagulant is being added to the water.

In the so-called solids contact type of treatment, incoming water, shortly after dosing with the treatment chemical, is conducted through a high concentration of the settled solids. Thus, a maximum concentration of preformed solids is immediately available for floc contact.

Effect of Mixing

Two stages of mixing or other means to create turbulence are generally used in a water plant. Rapid mixing to distribute the coagulant throughout the water being treated is frequently called "flash mixing." This rapid mixing is essential to uniformly disperse the coagulant and to promote collisions of coagulant particles with turbidity particles. The devices and mechanical equipment needed to obtain the required rapid agitation are described in Chapter 4. Such high turbulence conditions should be maintained for 30 to 60 sec, at the end of which the coagulant has hydrolyzed and has been adsorbed on the turbidity particles.

The second stage of floc growth or flocculation is accomplished by gentle stirring. Immediately following the addition of coagulant and during the flash mixing step, coagulation and precipitation produce finely divided suspensions. In a quiescent fluid, Brownian movement and the differences in settling velocities of various-sized particles would result in ever-increasing size of floc. But floc growth by these means is exceedingly slow. Floc growth can, however, be hastened by stirring the water. This increases the number and opportunities for particle contacts by collision. The degree of agitation must be great enough to keep the floc particles suspended and in motion, but not so great that the floc is disintegrated by the shearing forces. This process is called "flocculation." Detention times as little as 10 min, but more frequently 30 to 60 min, are generally adequate to produce a floc that will settle in a reasonable time.

COAGULATION OF COLOR

Occurrence and Nature of Color

Color, in addition to turbidity, is a common constituent of some surface waters and must be reduced by the water plant. Although colloidal forms of iron and manganese are sometimes the cause of color in water, and although industrial waste discharges can cause discoloration of water, the most common cause is complex organic compounds originating from the decomposition of natural organic matter.

The U.S. Public Health Service Drinking Water Standards of 1962 have recommended a maximum limit for drinking waters of 15 color units measured on a platinum-cobalt scale. This limit is based principally on aesthetic considerations, as the materials responsible for natural color in water are not known to be physiologically harmful to humans. In practice, most municipal plants strive to maintain finished waters with color values of 10 units or less.

There have been numerous and continuing attempts to chemically define the nature of color in water. This goal has not yet been attained, and disagreement still exists among investigators as to certain aspects of the fundamental nature of color. It is generally agreed, however, that the organic compounds producing color in water are derived mainly from soil humus which, in turn, is produced by the decay of vegetation. Color comprises a broad category of organic compounds which are collectively termed "humic substances," which simply denotes a group of compounds having similar properties.

The properties of humic substances that are of particular interest in water treatment can be listed as follows:

1. Humic substances in water are polymers with widely varying molecular weights, ranging from less than 800 to as high as 50,000. This range of polymer sizes would characterize color as ranging from true solution for the lowest molecular weights to colloidal particles for the upper molecular weight range. In terms of particle size, one study reported that 90 per cent were larger than 3.5 mμ and about 10 per cent were larger than 10 mμ. This particle size range clearly characterizes color particles as colloidal and significantly smaller in size than clay particles that generally have diameters on the order of 1 μ.
2. Studies of the chemical nature of humic substances have shown the presence of a variety of chemical groups, such as hydroxyl, carboxyl, methoxyl, and quinoid groups, which confer hydrophilic properties to the particles. These groups are dominantly negative, and hence color particles are invariably negatively charged, with the magnitude of the charge dependent on the degree of ionization and consequently on the pH of the water.
3. These properties of small size, hydrophilic nature, ionogenic groups, and strong negative charge dictate a mechanism of removal entirely different from removal of turbidity.

Coagulation of Color

Several characteristics of the removal of color by coagulation indicate that the mechanism is entirely different from that for the removal of turbidity. Whereas clay turbidity is best removed within a pH range of about 6.5 to 7.5, color removal is generally obtained at acid pH's of about 4 to 6. The dosage of coagulant is closely dependent on the initial concentration of color, in contrast to only slightly increased coagulant required for increasing concentrations of turbidity. It is also significant that zeta potential (always measured and frequently expressed as electrophoretic mobility) is closely correlated with residual color concentration. At the optimum pH, residual color decreases proportionately with increase in coagulant dose.

The relationships between pH, alum dosage, color removal, and zeta potential (expressed here as particle mobility) are given in the series of graphs shown in Fig. 6.

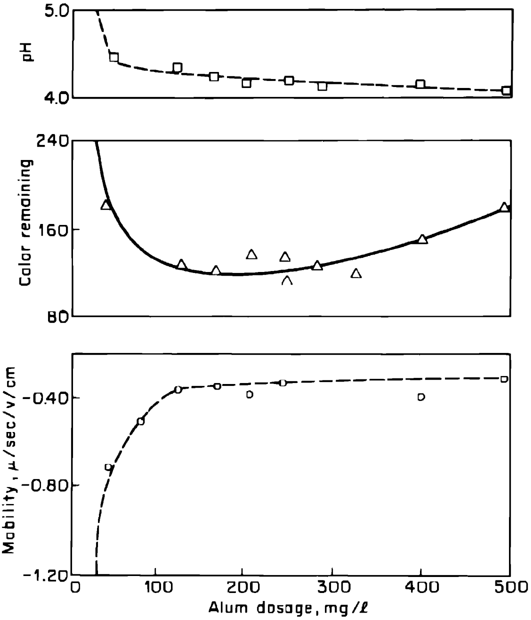


Fig. 6a Effect of alum dosage on coagulation of colored water. Curves show the effect of alum dosage on floc mobility, color removal, and pH. Color removal was poor with all dosages, the best sample showing a residual color of 120 units.

In Fig. 6*a*, varying doses of alum up to 500 mg/l were added to a colored water; the pH varied from about 4.5 with the lowest dose to 4.2 with the highest. Electrophoretic mobility of the floc particles is seen to rise from its most negative value and level off at a negative mobility of about —0.30. Some color removal was obtained under these conditions but was entirely inadequate.

The significant effect of pH on the removal of color from this water is shown in Fig. 6*b*, where the alum dosage was maintained at a constant 120 mg/l. The upper curve of color removal shows a narrow pH range of 5.0 to 5.7, within which good color removal was obtained. As the pH increased, negatively charged floc particles became positively charged slightly before the optimum pH, and then the mobility curve reversed its direction and crossed the line of electrical neutrality at almost exactly the center of the pH zone of optimum coagulation and color removal.

Figure 6*c* determines the minimum alum required for color removal, with the pH maintained constant at about 4.85. Color was increasingly removed as the dose of alum was increased. Color removal approaching the limiting residual color was obtained with 90 mg/l alum, and this dose coincides almost exactly with the point at which the particle mobility crossed the zero line.

Because the optimum pH for removal of color is generally not the optimum pH for minimum solubility of coagulant, the water after treatment with coagulant for color removal should be adjusted to a pH generally greater than 6.0 just prior to filtration. Under these conditions residual iron or aluminum can be maintained at values of less than 0.05 mg/l. There will, of course, be a need to further adjust the pH upward before distribution to minimize corrosion in the system.

Mechanism of Color Removal

The mechanism of removal of color can more properly be regarded as a process of chemical precipitation rather than coagulation. This significant difference is due entirely to the inherent differences between particles causing turbidity and those responsible for color. As described earlier, the electrical charge on a hydrophobic particle like clay generally is the result of adsorption of foreign ions onto the surface; the charge on the hydrophilic color particles, on the other hand, is due to ionogenic chemical groups which are an integral part of the compounds. These groups, such as carboxyl,

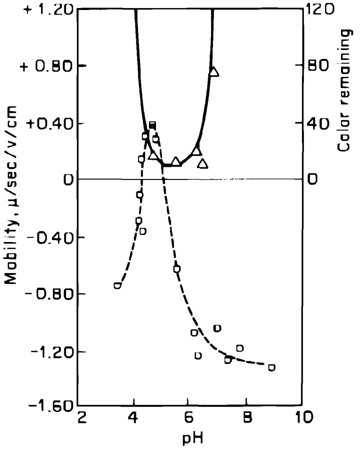


Fig. 6b Effect of pH on coagulation of colored water with constant alum dosage. A constant alum dosage of 120 mg/l was used, and pH was adjusted with $Ca(OH)_2$. Excellent color removal was obtained within a narrow pH zone of 5.0–5.7. Particle charge first decreased, then reversed almost exactly at the beginning of the pH zone of optimum color removal.

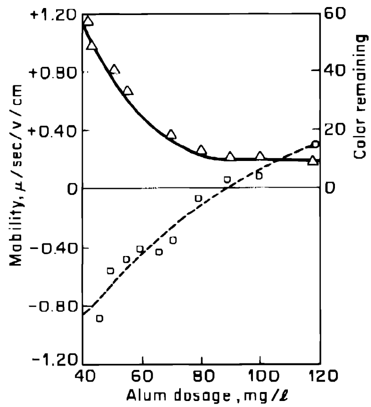


Fig. 6c Effect of alum dosage on coagulation of colored water at constant pH. The pH was mountained constant at 4.85 with addition of HCl or $Ca(OH)_2$, while alum dosage was varied. Color reduction was increased as alum dosage was increased. Particle-charge reversal occurred almost exactly at the alum dosage for optimum color removal.

hydroxyl, and others, determine the charge on the particle, and the charge depends on the degree of ionization, which in turn is influenced by the pH of the water. There is strong evidence that a chemical interaction occurs between the partially hydrolyzed iron or aluminum coagulant and some acidic group on the color molecule, forming an insoluble basic salt. The insolubility of the basic salt causes a precipitation removing from solution both the color and coagulant compounds. The slight solubility of certain salts of color compounds and coagulant is frequently responsible for some of the color remaining even after optimum conditions are obtained for its removal.

FLOCCULATION (COAGULANT) AIDS

Need for Aids

Difficulties with the coagulation process in water treatment have historically spurred the search for methods or chemicals which would overcome these problems. These problems take a variety of forms, many of which can be ascribed to deficiencies in the coagulation and flocculation process when under chemical or physical stress. Some symptoms of the difficulties have been small and slow-settling flocs during low-temperature coagulation, slow-settling flocs produced in low-mineralized colored waters, fragile flocs that are fragmented under hydraulic forces in basins and sand filters, and inability to obtain clarification in the presence of interfering substances.

In addition to the need to overcome coagulation problems, there has also been a continuing desire to improve the process by forming flocs with such desirable characteristics as rapid settling and toughness. With improved settling or toughness of flocs, plants have been able to increase water production with the existing physical plant, in some cases avoiding construction of additional plant capacity. A great variety of materials have already been made available to the water plant operator to successfully cope with some of his problems, and additional materials undoubtedly will become available in the future.

Definition

It has been general practice in this country to label the "aids to coagulation" as coagulant aids when in fact most of the compounds in current use are more properly flocculation aids. Coagulation refers to particle destabilization by the reduction of the repulsive potential of the double layer surrounding the particles, whereas flocculation implies a chemical bridging mechanism that enmeshes the particles in a three-dimensional network. Some of the "coagulant aids" do not benefit flocculation directly but are useful either in reducing interference from organic materials or in improving settling characteristics by increasing the density of the floc.

Materials

A great variety of materials have been used to aid clarification. The choice of one from the many available sometimes can be made on the basis of the particular physical or chemical property of the floc that needs to be altered. More frequently, the choice is empirical and must be based on the particular water being treated. The most widely used materials may be roughly classified as: (1) oxidants, (2) adsorbents-weighting agents, (3) activated silica, and (4) polyelectrolytes.

Oxidants

Difficulties with clarification or color removal which may arise from dissolved organic compounds often can be eliminated or minimized by the use of oxidants. The most common oxidant is chlorine added in sufficient amounts to obtain a "breakpoint." In this procedure, sufficient chlorine is added to satisfy the chlorine demand, at which time interfering organic material may be oxidized to innocuous compounds. Other less widely used oxidants are chlorine dioxide, ozone, and potassium permanganate. All of these chemicals must, of course, be added prior to coagulation when their function is to aid coagulation.

Adsorbents–Weighting Agents

Bentonitic clays are frequently used in treating waters containing high color, low turbidity, and low mineral content. The floc produced from highly colored waters by iron or aluminum coagulants is frequently too light to settle readily, i.e., the difference in specific gravity of the water and the floc is too small to permit rapid settling. The addition of clay, which has a relatively high specific gravity, results in a "weighting action," and floc then settles rapidly. In addition to its weighting action, benefit may also be obtained from the known ability of clays to adsorb organic compounds. Furthermore the addition of clay to a low-turbidity water provides increased opportunity for particle collisions, resulting in rapid formation of settleable floc.

In practice it has been found that dosages of clay ranging from about 10 to 50 mg/l frequently can result in the formation of a good and rapidly settling floc, effect a better removal of color and other organic matter, and broaden the pH range required for coagulation. The exact dosage for any given water must, of course, be determined by appropriate testing.

Other weighting agents besides clay have been used, such as powdered silica, limestone (which provides alkalinity in addition to its weighting action), and activated carbon (which possesses the additional advantage of high adsorptive capacity).

Activated Silica

Until the advent of synthetic polyelectrolytes, activated silica occupied a special position in chemical treatment of waters in that it was the only chemical available which could markedly aid the coagulation-flocculation process. In 1937, Baylis and, independently, Graf and Schworm discovered that the addition of silica in the form of a partially neutralized sodium silicate solution had a pronounced effect on a coagulation with alum. The use of this material, which became known as "activated silica," as an aid to coagulation developed rapidly from these discoveries. Actually, as early as 1920, O. M. Smith had experimented with the use of silicic acid, and because of the poor results he obtained, the process was ignored by the water field. The use of colloidal silica has now become widespread.

The source of colloidal silica is sodium silicate, which in itself is not a flocculation aid but becomes so when part of the alkalinity is neutralized by an acid, at which time it is considered to be "activated." Because the exact nature of this reaction is not known, it is not surprising that the process has more art than science. It is generally conceded that, for activation, three steps are required:

1. A concentration of sodium silicate solution on the order of 1.5 to 1.78% SiO_2 must be neutralized by an acid to the extent of 80 to 85 per cent of its alkalinity. Because silicic acid is a very weak acid, a great variety of acids can be and have been employed as the neutralizing agents. Some of them are: sulfuric acid, hydrochloric acid, ammonium sulfate, alum, chlorine, sodium bicarbonate, carbon dioxide, sodium silicofluoride, and others.
2. The partially neutralized solution is generally aged for a variable period of time. The time ranges from as little as 5 to 10 min to as much as 2 hr, although there does not appear to be any merit to the latter. Aging longer than 2 hr runs the risk of solidification of the entire solution by gelation.
3. To reduce the hazard of gelation, the silicate solution is generally further diluted to about 0.5 to 1.3% SiO_2 before being fed into the water to be treated. More recently these steps for activating silica have been automated by commercially available equipment to continuously generate activated silica.

Activated silica is normally used with aluminum coagulants, and the dose, expressed as mg/l of SiO_2, is sometimes determined as a proportion of the coagulant dose. There does not appear to be any basis for any fixed ratio of activated silica to alum, although the optimum dose does vary directly with alum dose at any fixed pH. Current practice is to use between 7 and 11 per cent of the alum dose. It should be pointed out that use of an excess of silica can be detrimental to flocculation.

There does not seem to be any general agreement on whether silica should be added before or after alum. Both methods have been used successfully, although the latter method is the more widely used.

Depending on the conditions of its use, such as pH and order of addition, activated silica can provide considerable benefits. It offers the advantages of: increased rate of coagulation, reduced coagulant dose, and extended pH range of optimum coagulation. It can also increase the rate of flocculation, produce larger and denser and hence faster-settling flocs, and toughen the floc so that filtration is improved. Other advantages are: more effective coagulation at low temperatures, improved removal of color, improved flocculation of high-turbidity waters, and reduction of colloidal matter passing filters.

Activated silica has also been found to be particularly effective as a filter aid. In this application, dosages of less than 1 mg/l SiO_2 have so toughened the floc that increased filtration rates can be used and longer filter runs can be obtained, reducing at the same time the amount of floc passing through the filters. Activated silica also finds wide application as the sole coagulant in softening operations.

Against this impressive array of advantages some disadvantages must be mentioned. Preparation of the silica sol requires precise control to obtain an active solution which will not gel; without careful control very large flocs may be produced, but residual turbidity may be objectionably high; very short filter runs may result from clogging of the upper layers of the filter; and overdosing with silica can inhibit rather than aid flocculation. And, as with all aids, activated silica may be effective with some waters and without any beneficial effects on others.

The exact nature of the silicon compound formed during activation and its behavior as a coagulant-flocculant aid is largely unknown. Some evidence suggests that during activation, both linear and cyclic polymers are formed. These polymers are then capable of entering the aluminum hydrolysis complex by replacing hydroxide ions. Under those conditions it behaves as a coagulant aid. In other instances the polymer by virtue of its great length can physically adsorb onto the floc and form "bridges" between particles and thus behaves as a flocculation aid.

Polyelectrolytes (Polymeric Flocculants)

Until the recent introduction of natural and synthetic materials called "polyelectrolytes" there was no serious competitor to activated silica for water clarification. Because these compounds have the characteristics of both polymer and electrolyte, they have been called "polymeric electrolytes" or "polyelectrolytes." More recently, the term "polymeric flocculant" has been used. Some of these compounds have been found to be effective flocculation aids. Their use may seem to be a new development in the field of water treatment; the process is, in fact, very old. It has now become fairly clear that many natural organic compounds such as starch, starch derivatives, cellulose compounds, polysaccharide gums, and proteinaceous materials are useful flocculation aids. In spite of their varied sources, these compounds may be collectively described as biocolloids, which are characterized as naturally occurring polymers possessing a number of electrical charges (hydrophilic groups) along the molecular chain of carbon atoms.

Synthetic polymers have been produced which are analogous in general properties to the natural biocolloids. All of these compounds contain repeating units of small molecular weight, chemically combined to form a molecule of colloid size, and each of the repeating units carries one or more electrical charges or ionizable groups. The advantage of the synthetic polyelectrolytes over the naturally occurring types is that the molecule can be tailored to meet specific requirements. This, in fact, has been done by using various monomers or units with different ionizing groups and copolymerizing these materials to make a great variety of compounds.

All synthetic polyelectrolytes can be classified on the basis of the type of charge on the polymer chain. Thus polymers possessing negative charges are called "anionic," while those carrying positive charges are "cationic." Certain compounds carry no electrical charge and are called "nonionic polyelectrolytes." Because of the great variety of monomers available as starting material and the additional variety that can be obtained by varying the molecular weight, charge density, and ionizable groups, it is not surprising that a great assortment of polyelectrolytes are available to the water plant operator.

A major benefit obtained with polyelectrolytes is a very large increase in floc size. This enormous increase in floc size is illustrated by the pair of photomicrographs shown in Fig. 7. Figure 7*a* shows a normal alum floc of typical flocculant appearance. When 0.5 mg/l of an anionic polyelec-

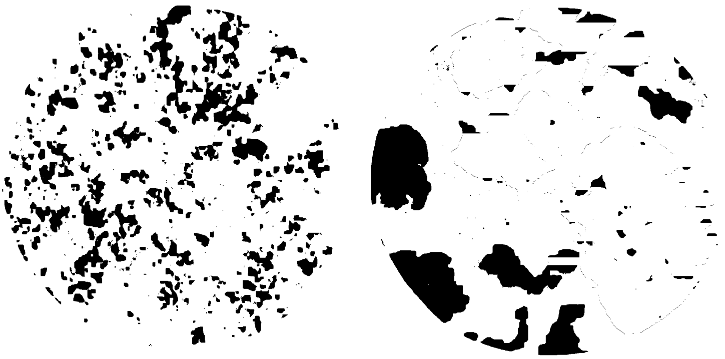


Fig. 7*a*, *b* Photomicrograph of alum floc with and without polyelectrolyte aid.

trolyte is added, the size of the floc is increased by several orders of magnitude, as shown in Fig. 7*b*.

Because of the greatly increased size of the floc, the settling rate of the floc is also greatly increased. This change in the physical characteristics of the floc can be illustrated by the settling curves shown in Fig. 8. The plot is turbidity remaining in per cent versus time (in minutes). The data were obtained by adding an anionic polyelectrolyte to an alum coagulation. It is readily apparent that 0.5 mg/l of polyelectrolyte produced a floc that was more than 95 per cent settled within 2 min. Only 50 per cent settled in 2 min when alum alone was used. Significantly, when the polyelectrolyte dose was increased to 2.0 mg/l, the coagulation was seriously inhibited, illustrating that there exists an optimum or "just right" dose, and that an excessive dose will produce a poor flocculation. In general, anionic polyelectrolytes behave as flocculation aids which modify the physical characteristics of floc produced by aluminum or iron coagulants. Tests have shown that the effectiveness of anionic polyelectrolytes is nearly independent of pH, alkalinity, hardness, and turbidity. However, the optimum dose of polyelectrolyte increases linearly with the alum dosage. The pH range of optimum alum coagulation is not extended.

In contrast to the anionic polyelectrolytes, the cationic types can perform as flocculants without the addition of metal coagulants, although this use generally results in rather high residual turbidity. When used with coagulants the cationic polyelectrolytes offer additional advantages: (1) they can reduce the alum or iron requirements; (2) they can reduce the interference to coagulation that substances such as tripolyphosphate and lignin create; and (3) they are capable of flocculating living organisms such as algae and bacteria.

The majority of the nonionic polyelectrolytes are derived from natural sources, such as starch and polysaccharide gums. In many instances, their overall cost, even though generally used in higher dosages, is less than the synthetics. Whether they will be useful for any particular water must be determined experimentally beforehand.

In practical terms, the use of polyelectrolytes provides a means of increasing the size and hence the settling rate of floc during periods of the year when flocculation becomes difficult because of water quality changes or because of the influence of low temperatures. Increased volumes of water can be treated in a given plant size, particularly when an upflow sludge-blanket type of equipment is being used. Polyelectrolytes have considerable advantage over activated silica, first in the ease with which feed solutions can be prepared and administered to the water, and second in the ease of storage, in that dosages of the order of 0.1 to 1.0 mg/l for the synthetic types and 1 to 10 mg/l for the naturally derived polymers are required.

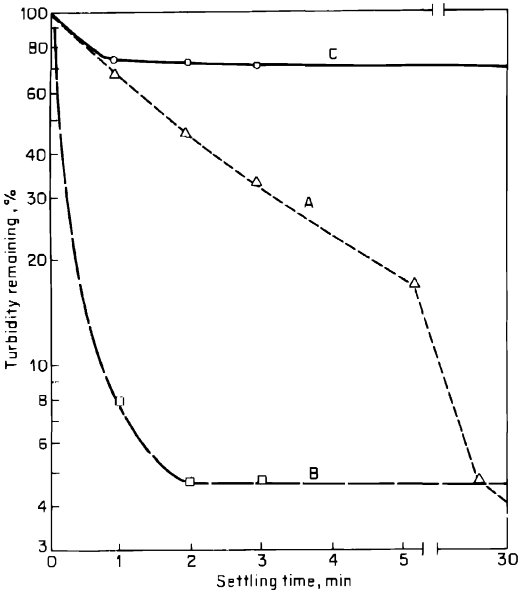


Fig. 8 Effect of an anionic polyelectrolyte on alum coagulation of a turbid water. Turbid water was flocculated with: Curve *A*, 10 mg/l of alum; curve *B*, 10 mg/l alum plus 0.5 mg/l of an anionic polyelectrolyte; and curve *C*, 10 mg/l of alum plus 2.0 mg/l of an anionic polyelectrolyte. Settling rate of floc was greatly increased with a 0.5 mg/l dosage, but dispersion was obtained with 2.0 mg/l of polyelectrolyte.

As with activated silica the preferred order of addition of the polyelectrolytes varies with the particular water. Generally, the polymer is added as a dilute solution with the metal coagulant or shortly thereafter. Efficient mixing must be provided to ensure quick dispersal of the coagulant and polymer. In some applications it may be beneficial to use both anionic and cationic polyelectrolytes, each being added to the water separately and the dosages being controlled by zeta-potential measurements.

Polyelectrolytes have also been used as filtration aids, in which the polymer is added to the coagulated and settled water immediately prior to sand filtration. This use depends, in part, on the ability of the polymer to form a tough floc that will resist fragmentation by hydraulic shear stresses. In this application, very small dosages of polyelectrolytes, frequently on the order of 50 to 100 parts per billion, permit higher filtration rates and reduce the hazard of floc breaking through the filter.

An extensive technical literature has attempted to describe the mechanism of how polyelectrolytes perform their functions. While there is still some disagreement on detail, it is generally conceded that a polyelectrolyte is a molecule with a high molecular weight, ranging on the order of 50,000 to several million. The cationic types are generally smaller than the anionics. Molecular weights on this order result in a threadlike particle whose greatest dimension, its length, can be measured in terms of a fraction of a micron to as much as 10 μ. The polyelectrolyte assumes a "stretched-out" shape in solution because of the electrostatic repulsion between adjacent charged groups along the carbon backbone of the molecule as contrasted to an uncharged polymer, which forms a random coil.

The extremely long length and the high charge density of the molecule are important characteristics for the theory of how polyelectrolytes behave. It is now generally agreed that a "bridging" mechanism accounts for the flocculation behavior of these compounds. In its simplest form, the theory postulates that the polymer molecules attach themselves to the surface of the suspended particles at one or more sites and that part of the long chain extends out into the bulk of the solution. The free end of the molecule is then able to adsorb onto another suspended particle when contact is made, thus forming a "bridge" or "link" between two particles of turbidity. This process is a dynamic one in which adsorption and desorption are rapidly taking place until a condition is established in which almost all of the polymer segments become attached by one or more sites to two or more turbidity particles. The reactions are very fast, approximately 85 per cent of the polymer being adsorbed within about 10 sec with an additional 10 per cent becoming attached after a more prolonged contact. In addition to adsorption, the process of hydrogen bonding has been suggested as a mechanism for the attachment of polymer segments to particle surfaces. The progressive linking of more and more particles results in an ever-increasing size of floc whose eventual size is limited by its ability to withstand the hydraulic shear gradient imposed upon it by agitation or turbulence. Theoretical and experimental evidence has shown that optimum flocculation will be obtained when the surface of the turbidity particle is partially occupied by adsorbed polymer. Some studies have shown that the maximum flocculation rate is obtained when the turbidity particles have one-half their surfaces covered with polymer segments. If too many adsorption sites are occupied by polymer segments, bridging will be restricted, and if all sites are occupied, bridging will be impossible, both conditions leading to a dispersed rather than a flocculated system. Conversely, if too few sites are occupied by polymers, the possibility of bridging between adjacent particles will be reduced, and bonds may be so weak that the floc will be unable to withstand shearing forces. Rapid mixing promotes interparticle bridging by the polyelectrolyte rather than intraparticle adsorption. This theory, then, offers an explanation as to why an optimum range of polymer dose exists where too little leads to a weak flocculation, and too much results in a dispersion. As a consequence of the very high charge density on a polymer, the small dosages commonly used can drastically alter the zeta potential.

The remarkable effectiveness of polyelectrolytes in flocculation, even at the low dosages commonly used, is comprehensible since the number of polymer molecules in solution even at low dosages exceeds by several orders of magnitude the number of colloidal and suspended particles likely to be present in water. A dosage of 1 mg/l of a polyacrylamide polyelectrolyte with a molecular weight of about 5.5×10^6 (5.5 million) yields about 1×10^{14}(100 trillion) polymer segments in each liter of water, more than enough to provide hundreds of polymer molecules for each particle of turbidity.

Since polyelectrolytes are being used to treat municipal water supplies, the question of toxicity has had to be considered. This is particularly relevant for the synthetic polymers which are manufactured from monomers that are, in some cases, relatively toxic; and almost all commercially available polyelectrolytes contain a small percentage (<0.05 per cent) of residual monomer as an impurity. To provide assistance to the users and to the individual state and local health departments, the U.S. Public Health Service has established a procedure whereby commercial products are reviewed for approval for use in treating drinking water. Lists of approved products are published in the professional journals from time to time.

COAGULATION IN PRECIPITATION SOFTENING

In the lime softening process, precipitates of calcium and magnesium are formed which must be settled before filtration. In certain waters, particularly those low in magnesium, the precipitates may be so fine as to approach colloidal sizes, in which case a coagulant or coagulant aid must be added to aid in the sedimentation. The common aluminum and iron salts are frequently used for this purpose, generally in dosages of about 10 mg/l or less. But since these salts increase lime requirements and add noncarbonate hardness, it has become common practice to use sodium aluminate, which functions as both a coagulant and a softening agent by virtue of the excess sodium hydroxide in the commercial product. Dosages of the order of 5 mg/l are commonly used.

Activated silica has been used extensively in softening as a primary coagulant. For this purpose, the activated silica is generally added prior to the lime, although there appear to be exceptions to this for some waters. Dosages generally range from 2 to 5 mg/l.

Polyelectrolytes, both anionic and cationic, can be used in softening but as yet they are not as widely used as activated silica.

DOSAGE AND PROCESS CONTROL

The quality of treated water and the costs of chemicals for its production are dependent on proper control of the coagulation-flocculation processes. Laboratory and in-plant control are essential to proper coagulation treatment for two basic reasons: first, plants which employ coagulation usually treat surface waters which may be subject to wide variations in quality and are much more likely to be contaminated than well supplies; and second, the best and most economical treatment of such waters cannot be predicted from known relationships but must be checked by one or more testing or monitoring techniques. The coagulation and flocculation of water is influenced by a number of interrelated factors such as pH, color, turbidity, mineral content and composition, temperature, the duration and degree of agitation during flocculation, and finally, the characteristics of the coagulant or flocculation aid in use. Unfortunately, the optimum conditions for coagulation cannot be determined from the results of a chemical and physical analysis of the water, but must be determined empirically. The type and frequency of tests depend largely on the character of the raw water and on the plant design. Where possible, laboratory investigations of treatment should begin before the plant is designed and constructed, since operation and control can be simplified if the plant is designed specifically to handle a particular raw water, especially if that water is subject to wide variations in quality. Because each water plant may require its own specialized combination of tests and methods for performing these tests, the subject of dosage and process control will be treated here only in a general way.

The single most widely used test to determine dosage and other parameters is the "jar test." The equipment for this test and the directions for proper performance have been published. The jar test attempts to simulate the full-scale coagulation-flocculation process and has remained the most common control test in the laboratory since its introduction in 1918. Since the intent is to simulate an individual plant's conditions, it is not surprising that there has been no standardization of the test. The jar test as variously performed does, however, have some elements of conformity. In its essentials, the jar test simply consists of a series of sample containers, the contents of which can be stirred by individual mechanically operated stirrers. Water to be treated is placed in the containers, and the treatment chemicals are added while the contents are being stirred. The range of conditions, for example pH and coagulant dosages, are selected to bracket the anticipated optima. After a short (1- to 5-min) period of rapid stirring to ensure complete dispersion, the stirring rate is decreased, and flocculation is allowed to continue for a variable period, 10 to 30 min or more, depending on the simulation. The stirring is then stopped, and the flocs are allowed to settle for a selected time. The supernatant is then analyzed for a variety of parameters.

The interpretation of the results of this test requires some determinative measure of the flocculation. A number of approaches have been used: (1) visual evaluation of floc size, (2) visual or photometric measurement of supernatant clarity or color, (3) time of appearance of first floc, (4) chemical determination of residual coagulant in supernatant, (5) rate of settling of flocs, (6) measurement of the electrophoretic mobility (zeta potential) of the particles, and (7) more recently, the filterability characteristics either through paper, membranes, or miniaturized sand filters.

Since the objective of coagulation-flocculation is to destabilize the particles so that removal can be obtained by sedimentation and filtration, residual turbidity measurement has been a most important parameter. Turbidity, as the word is understood in the water field, is simply an optical property of the suspended particles in the water, and it is not a direct assessment of the quantity present. Since the measured optical properties of particles vary depending on their size distribution, refractive index, concentration, angle of observation with respect to the light source, and the instrument geometry, it is not surprising that numerical values for turbidity may not be compared between plants. The problem is further complicated because of the lack of generally accepted turbidity reference material. In the usual determination of turbidity, the light scattered by the particles in the water is compared with that scattered by a dilute clay suspension, which in turn is standardized by the Jackson candle method. The problem here is that the Jackson candle method cannot be used for turbidities less than 25 units and that clay suspensions are neither standard nor reproducible among laboratories. There are ongoing efforts to standardize this test particularly for the low turbidities of interest to the water plant. The direction of the effort is toward a standardized instrument geometry and some standardized reference material.

Measurement of zeta potential is another procedure useful for control of the coagulation process and for evaluating the results of the jar test. Zeta potential of particles is never determined directly, but is calculated from a measurement of particle electrophoretic mobility. In the usual procedure, a special apparatus is used with which the behavior of particles can be observed microscopically. Under the influence of an applied voltage, the charged particles will migrate to the poles of opposite polarity; the particle velocity can be measured by noting the time that it takes particles to traverse a known distance. From these and other data it is possible to calculate both electrophoretic mobility and zeta potential. The numerical value of the zeta potential that indicates optimum coagulation varies with the type of colloid to be removed from the water. As pointed out earlier, removal of organic colloids, such as color, is generally obtained at zeta potentials near zero, whereas optimum clay turbidity removals are obtained when zeta potentials are slightly negative, ranging from —10 mv to perhaps —5 mv. But since a water may very likely contain a heterogeneous mixture of colloid types, the precise zeta potential which signals a good coagulation must be established for each water by other methods such as the jar test or by correlation to actual plant performance.

Within a plant, manual or continuous monitoring of turbidity or color are commonly used to monitor the filtered water. The test may be applied to either the settled water or to the filtered water or to both.

Another method of evaluating the particle content of the water is the "cotton plug" technique which was first described by Baylis. Small cotton filters are installed in a bypass of the plant's filter effluent line, and varying quantities of water are filtered, after which the cotton is ashed and the inorganic residue weighed. Media other than cotton have been used such as filter paper, glass fiber, and organic membranes, with the latter finding common use to measure residual color or turbidity. While this technique will not aid directly in controlling the hourly coagulant dose, it can contribute to the long-term knowledge of the performance of the plant.

Analysis for residual coagulant (aluminum or iron) may be used to indicate the efficiency with which the filters are removing flocs, which in turn is related to flocculation. As with suspended-solids determination, this test is not useful for the short-term control of the plant, but can provide useful information over the long term.

Other tests commonly used either to control or monitor the treatment process are pH, alkalinity, and length of filter runs. A recently developed control test is to continuously divert a small flow from the rapid-mix process and apply it to a small filter. Turbidity can be monitored on the filtrate, and because the filtration and turbidity measurement can be completed within a short time, the optimum dosage can be arrived at rapidly enough to make the appropriate dosage alterations in the full-scale plant. This control test has found its greatest usefulness in monitoring those plants that differ considerably from the conventional water-treatment plant. The modification essentially consists of eliminating flocculation and sedimentation basins and permitting these unit processes to occur in a specially designed filter. The filter contains two and sometimes three kinds of media of such porosity that sufficient storage is provided for the flocs produced in the flocculation. Coagulant- and flocculation-aid dosages in the full-scale plant can be adjusted from the results continuously obtained on the small monitor filter.

Automation, which has been extensively applied to numerous manufacturing plants, has found relatively little application in coagulation control, largely because of the lack of a fundamental or systematic relationship between coagulation and any one measurable process variable. But undoubtedly this deficiency will be corrected as new information and techniques become developed.

METAL COAGULANTS

The coagulants that are commonly used in water treatment are: (1) those based on aluminum, such as aluminum sulfate, ammonia, and potash alum and sodium aluminate, and (2) those based on iron, such as ferric sulfate, ferrous sulfate, chlorinated copperas, and ferric chloride.

In the following sections some of the relevant chemical and physical properties of the common coagulants are described. In addition, the chemical interactions of coagulants with the more important water constituents are also given. These reactions are presented here in the form of chemical equations with the full knowledge that these equations do not represent exactly what happens in water. It has already been shown that the hydrolysis of iron and aluminum salts is far more complicated than these equations indicate. Nevertheless, these equations are useful in the form they are presented to indicate in an approximate way the products of the reactions and the quantitative relationships.

Aluminum Sulfate. Aluminum sulfate, $Al_2(SO_4)_3 \cdot 18\ H_2O$, as a commercial product is also commonly known as alum, filter alum, alumina sulfate, etc., and is by far the most widely used coagulant. Commercial alum or filter alum differs from the pure reagent and has no exact composition. It contains a slight excess of alumina and less water of crystallization than indicated by the chemical formula. Filter alum contains 17 per cent water-soluble Al_2O_3 (the theoretical content of reagent $Al_2(SO_4)_3 \cdot 18\ H_2O$ is 15.3 per cent) and about 14 moles of water of crystallization. It is available in lump, ground, or powdered forms as well as a concentrated solution. It is readily soluble in water and is easily applied as a solution or as a dry material.

Reactions between alum and the natural constituents of various waters are influenced by many factors; hence it is impossible to predict accurately the amount of alum that will react with a given amount of natural alkalinity or of lime or soda ash added to the water. Hypothetical reactions, however, can be written which will serve as a general guide.

The simplest case is the reaction of Al^{+++} with OH^- ions made available by the ionization of water or by the alkalinity of the water. Solution of alum in water produces

$$Al_2(SO_4)_3 \cdot 14\ H_2O = 2\ Al^{3+} + 3\ SO_4^{2-} + 14\ H_2O$$

Hydroxide ions become available from ionization of water.

$$H_2O = H^+ + OH^-$$

The aluminum ions (Al^{3+}) then react:

$$2\ Al^{3+} + 6\ OH^- = 2\ Al(OH)_3$$

Consumption of hydroxide ions in the water will result in a decrease in the alkalinity. Where the natural alkalinity of the water is inadequate for the alum dosage, then added alkalinity must be supplied in the form of hydrated lime, soda ash, or caustic soda. The reactions of alum with the common alkaline reagents are shown in Table 3-2. While these reactions are an oversimplification of what actually takes place, they do serve to indicate orders of magnitude and to point out that sulfate ion is added to the water and that CO_2 may be formed unless lime or caustic soda is added to the water.

TABLE 3-2 Hypothetical Reactions of Aluminum Sulfate

$$Al_2(SO_4)_3 \cdot 14\ H_2O + 3\ Ca(HCO_3)_2 = 2\ Al(OH)_3 + 3\ CaSO_4 + 6\ CO_2 + 14\ H_2O$$

$$Al_2(SO_4)_3 \cdot 14\ H_2O + 6\ NaHCO_3 = 2\ Al(OH)_3 + 3\ Na_2SO_4 + 6\ CO_2 + 14\ H_2O$$

$$Al_2(SO_4)_3 \cdot 14\ H_2O + 3\ Na_2CO_3 = 2\ Al(OH)_3 + 3\ Na_2SO_4 + 3\ CO_2 + 14\ H_2O$$

$$Al_2(SO_4)_3 \cdot 14\ H_2O + 6\ NaOH = 2\ Al(OH)_3 + 3\ Na_2SO_4 + 14\ H_2O$$

$$Al_2(SO_4)_3 : 14\ H_2O + 3\ Ca(OH)_2 = 2\ Al(OH)_3 + 3\ CaSO_4 + 14\ H_2O$$

In terms of quantities, the reactions in Table 3-2 can be expressed as follows:

1 mg/l of alum reacts with:

- 0.50 mg/l natural alkalinity, expressed as $CaCO_3$
- 0.33 mg/l 85% quicklime as CaO
- 0.39 mg/l 95% hydrated lime as $Ca(OH)_2$
- 0.54 mg/l soda ash as Na_2CO_3

These above approximate amounts of alkali when added to water will maintain the alkalinity of the water unchanged when 1 mg/l of alum is added. For example, if no alkalinity is added, 1 mg/l of alum will reduce the natural alkalinity by 0.50 mg/l as $CaCO_3$, but alkalinity can be maintained unchanged if 0.39 mg/l of hydrated lime is added. This lowering of natural alkalinity is desirable in many cases to attain the pH range for optimum coagulation of turbidity. In fact, it is frequently more economic to add sulfuric acid as an acidifying chemical than to use the acid properties of alum.

Liquid Alum. In recent years "liquid alum," which is a concentrated solution of alum in water, has become generally available and may be more economic to purchase when the water plant is within trucking distance of the alum manufacturing plant. Liquid alum contains 5.8 to 8.5 per cent water-soluble alumina (Al_2O_3) as against 17 per cent for crystallized alum, but is lower in price and convenient to transport, handle, store, and feed.

Sodium Aluminate. Sodium aluminate, $NaAlO_2$, differs from alum in that it is alkaline instead of acid in its reaction. The composition varies somewhat, but in general it contains about 88 per cent of $NaAlO_2$, the remainder being largely excess caustic soda and some sodium carbonate.

Sodium aluminate is rarely used alone, but generally with alum to obtain some special results: for example, in the "double coagulation" of highly colored waters, in which alum alone or alum and sulfuric acid are added to the raw water in the primary basin to coagulate the color colloids at the low pH range generally required for color coagulation. This results, however, in undesirable concentrations of soluble aluminum compounds; alkaline sodium aluminate is then added, also lime if needed, to increase the pH to at least 6.0, which causes the soluble aluminum to flocculate in a secondary settling basin. The reactions of sodium aluminate with alum and with free carbon dioxide produce insoluble aluminum compounds.

$$6\ NaAlO_2 + Al_2(SO_4)_3 \cdot 14\ H_2O = 8\ Al(OH)_3 + 3\ Na_2SO_4 + 2\ H_2O$$

$$2\ NaAlO_2 + CO_2 + 3\ H_2O = Na_2CO_3 + 2\ Al(OH)_3$$

Sodium aluminate is also used in lime-soda softening of water to coagulate the fine precipitates of calcium carbonate and magnesium hydroxide resulting from the softening reactions.

Sodium aluminate may be purchased either as a solid or as a solution. The cost of the material is high, but the required doses are small, so the treatment may be applied to advantage and at reasonable cost when special conditions justify it.

Potash Alum and Ammonia Alum. The formulas for these compounds are, respectively, $Al_2(SO_4)_3 \cdot K_2SO_4 \cdot 24\ H_2O$ and $Al_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 24\ H_2O$. Neither of these compounds is widely used in treating water, although ammonia alum is commonly used in treating swimming pool water. In this application the ammonia content is desirable to obtain chlorine-ammonia compounds for disinfection.

Ferric Sulfate. Ferric sulfate, $Fe_2(SO_4)_3$, is available as a commercial coagulant in the form of an anhydrous granular material that is readily soluble in water. Solutions are made by stirring one part by volume of ferric sulfate with two parts of water to produce a solution of about 40% ferric sulfate. This concentrated solution is then diluted to the desired concentration. The dilute solutions tend to hydrolyze and deposit ferric hydroxide.

Ferric sulfate reacts with the natural alkalinity of the water or with the added alkaline materials such as lime or soda ash. The reactions may be written to show precipitation of ferric hydroxide although in practice, as with alum, the reactions are more complicated than this. The reactions are shown in Table 3-3.

TABLE 3-3 Reactions of Ferric Sulfate

$$\begin{aligned}
Fe_2(SO_4)_3 + 3\ Ca(HCO_3)_2 &= 2\ Fe(OH)_3 + 3\ CaSO_4 + 6\ CO_2 \\
Fe_2(SO_4)_3 + 6\ NaHCO_3 &= 2\ Fe(OH)_3 + 3\ Na_2SO_4 + 6\ CO_2 \\
Fe_2(SO_4)_3 + 3\ Na_2CO_3 + 3\ H_2O &= 2\ Fe(OH)_3 + 3\ Na_2SO_4 + 3\ CO_2 \\
Fe_2(SO_4)_3 + 6\ NaOH &= 2\ Fe(OH)_3 + 3\ Na_2SO_4 \\
Fe_2(SO_4)_3 + 3\ Ca(OH)_2 &= 2\ Fe(OH)_3 + 3\ CaSO_4
\end{aligned}$$

In general ferric coagulants are useful over a wide pH range of 4.0 to 11.0. Ferric sulfate is also particularly successful when used for color removal at low pH values; at high pH values it may be used for iron and manganese removal and in the softening process. For the latter uses the insolubility of ferric hydroxides at high pH values makes ferric sulfate or the iron coagulants in general preferable to alum.

Ferrous Sulfate. Ferrous sulfate, $FeSO_4 \cdot 7\ H_2O$ (also commonly known as copperas), is available either as crystal or granules, both of which are readily soluble in water. (In some areas, a concentrated solution of ferrous sulfate is available at considerable savings in cost over the dry material.) Ferrous sulfate reacts either with the natural alkalinity of water or added alkalinity to form ferrous hydroxide, $Fe(OH)_2$. But since ferrous hydroxide is quite soluble, it must be oxidized to ferric hydroxide, which has a negligible solubility, in order to be useful. At pH values above 8.5, oxidation may be accomplished by (1) aeration, (2) the dissolved oxygen in the water, or (3) adding chlorine. In the first two cases, lime must be added to obtain sufficient alkalinity.

Each mg/l of $FeSO_4 \cdot 7\ H_2O$ added requires theoretically about 0.03 mg/l of oxygen to obtain ferric hydroxide; thus surface waters generally will contain sufficient oxygen to oxidize 100 to 200 mg/l of ferrous sulfate dosages. In practice, it would be undesirable to deplete the oxygen in the water. The dose of lime required to obtain the necessary alkalinity is approximately 0.27 mg/l of 95% hydrated lime for each 1.0 mg/l of ferrous sulfate.

The important reactions for ferrous sulfate are:

$$FeSO_4 \cdot 7\ H_2O + Ca(OH)_2 = Fe(OH)_2 + CaSO_4 + 7\ H_2O$$

$$4\ Fe(OH)_2 + O_2 + 2\ H_2O = 4\ Fe(OH)_3$$

Ferrous sulfate and lime find their greatest use in coagulations that must be conducted at high pH values, for example, in lime-soda softening of water and in iron and manganese removal.

Chlorinated Copperas. When chlorine is used to oxidize the ferrous hydroxide obtained from ferrous sulfate, the process is known as the "chlorinated copperas" treatment. In contrast to the high pH values required for oxidation by oxygen, chlorine will react over a wide pH range.

In practice ferrous sulfate and chlorine are fed separately and are generally mixed just prior to entry into the coagulation system. Theoretically, each mg/l of ferrous sulfate requires 0.13 mg/l of chlorine, although additional chlorine is generally added to ensure complete reaction and to provide chlorine for disinfection. The reaction with chlorine produces ferric sulfate and ferric chloride.

The reaction is as follows:

$$6\ FeSO_4 \cdot 7\ H_2O + 3\ Cl_2 = 2\ Fe_2(SO_4)_3 + 2\ FeCl_3 + 7\ H_2O$$

Coagulation with chlorinated copperas is especially useful in plants where prechlorination is required. It has a further advantage over ferrous sulfate in that coagulation can be obtained over a wide range of pH values, 4.0 to 11.0.

Ferric Chloride. Ferric chloride finds only very limited use in water treatment. It is available commercially in liquid, crystal, and anhydrous forms. The liquid and crystal forms are very corrosive and must be handled in rubber-lined tanks or in glass. The anhydrous form can be handled in steel only so long as moisture is excluded. Because ferric chloride is very hygroscopic, drums must remain sealed until needed, and their entire contents must be dissolved in water at one time.

The reactions of ferric chloride with natural or added alkalinity can be shown as follows:

$$2\ FeCl_3 + 3\ Ca(HCO_3)_2 = 2\ Fe(OH)_3 + 3\ CaCl_2 + 6\ CO_2$$

$$2\ FeCl_3 + 3\ Ca(OH)_2 = 2\ Fe(OH)_3 + 3\ CaCl_2$$

Ferric chloride is an acid salt and will consume alkalinity when added to water. The quantities of alkalinity can be expressed as follows:

1 mg/l of ferric chloride reacts with:
  0.92 mg/l of natural alkalinity, expressed as $CaCO_3$
  0.72 mg/l 95% hydrated lime

SUMMARY

Removal of suspended solids from water by sedimentation, flocculation, and filtration has an ancient heritage. And it has been only within the last 50 years that water treatment has progressed from an art to a technology that is based on scientific principles. It is now generally recognized that coagulation and flocculation are a specialized branch of colloid chemistry, itself a branch of physical chemistry, that considers the behavior and properties of small particles. The very small size and great numbers of particles in water make the surfaces of these particles much more important than the weight of the particles. Thus, interfacial or colloid properties dominate in the coagulation and flocculation processes.

Surfaces of particles either contain or acquire electrical charges that lead to forces that cause particles to be repulsed or attracted. Moreover, other forces, such as the Van der Waals force, inherent in the atomic structure of matter, also become involved. As the result of the presence of electrical charges and in order to maintain electrical neutrality, particles are surrounded with a shell of ions of opposite charge, generally described as the electrical double layer. Such suspensions are completely stable for very long times so long as no external influences are added to the colloid system. Instability, leading to agglomeration, is readily produced by such external influences as metal coagulants, polyelectrolytes, and mixing.

The process of coagulation and flocculation is sensitive to many variables such as pH, coagulant dose, concentration, and kind of anions, to mention just a few. Of the many variables that can be controlled by the water plant operator, that of pH adjustment is the single most important. But to obtain the most efficient removal of particles, other conditions as well as pH must be controlled.

Several mechanisms have been proposed for the removal of particles by metal coagulants and polymers, such as electrical double-layer compaction, neutralization of electrical charges, adsorption and bridging, and mechanical enmeshment. It seems likely that all of these processes may be involved in varying degrees in any coagulation-flocculation system.

An understanding of the mechanism of the coagulation-flocculation process was significantly enhanced by the recent knowledge of how metal coagulants behave in aqueous solution. Thus, the simple concept of the formation of aluminum or ferric hydroxide has been supplanted by the far more complicated chemistry of the hydrolysis products of these compounds. While a better understanding of colloid chemistry and chemical hydrolysis of coagulants has provided the means to interpret what happens in a coagulation, it has not, unfortunately, been able to provide the means to predict. Thus the practical water plant operator has had to rely on experimental techniques to guide him in the treatment of water. The jar test, with its many variants, still remains the most useful technique, although other techniques, such as turbidity monitoring, filtration devices, and electrophoretic mobility are being more widely adopted.

For the last several decades little progress was made in providing the water plant operator with other than the traditional coagulants based on aluminum and iron until the recent introduction of polyelectrolytes. While the ideal polyelectrolyte has not yet been discovered, it seems inevitable that these compounds will find greater and greater usefulness in the water plant of the future.

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4

Mixing and Sedimentation*

Revised by ROBERT S. GEMMELL

COAGULATION AND SEDIMENTATION

The distinction between mixing basins and sedimentation basins is the same as the distinction between the coagulation process and sedimentation process. As described in Chap. 3, coagulation involves the addition of chemicals to the water, their uniform distribution through the water, and the building up of a readily settleable floc, usually by prolonged agitation of the water. Coagulation is accomplished by appropriate equipment in three steps or phases of mixing, floc formation, and conditioning. The functional difference in these transitional steps is one of decreasing agitation. The initial high-speed mix ensures adequate, prompt dispersion of chemicals in the water being treated. The intermediate mix, at a lower speed, starts floc formation or coagulation, whereas the final mix is a gentle, slow movement that promotes further floc buildup and conditioning.

Sedimentation is the process by which coagulated or suspended matter

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separates from the water by subsidence and deposition. An effective means of water treatment, sedimentation does not depend upon coagulation but is made more effective by it. Long before the benefits of coagulation were known to waterworks men, plain sedimentation was in general use.

The following definitions should be noted:

1. *Rapid or flash mixing* is the process by which a coagulant is rapidly and uniformly dispersed through the mass of the water. This process usually occurs in a small basin immediately preceding or at the head end of the "coagulation basin."
2. *Flocculation* is the stimulation by mechanical means of the agglomeration of the suspended matter into compact, fast-settling flocs. This process usually occurs in the "mixing basin" or "flocculation basin."
3. *Sedimentation* is the separation by gravity of the flocculated solids from the water. This process occurs in the sedimentation basin, sometimes referred to as the "settling basin."

INTRODUCTION OF THE MIXING BASIN

The value of adequate coagulation was apparently not known to the early designers of rapid-sand filtration plants, although M. N. Baker[1] describes a plant, built by the Vicksburg, Miss., waterworks in 1887–1888, which included coagulation and sedimentation basins with a lateral-flow filter. George W. Fuller, at Louisville, apparently conducted all his experiments on the treatment of Ohio River water without giving consideration to mixing basins, for there is no reference to their use in his report.[2] Milton F. Stein, in the first edition of his work on water treatment,[3] presented a sketch of a mechanical filter plant which included only a settling basin and had no provision for coagulation basins. A review of waterworks literature, however, indicates that, after 1915, coagulation and sedimentation were used by most engineers in connection with rapid-sand filtration.

Mixing basins have come into wide use, as shown by Bean.[4] He reported that in the installations in service, built, or remodeled during the period 1922–1932, 10 per cent had no mix, 8 per cent had spiral flow, and the other 82 per cent were about two-thirds baffled and one-third mechanically agitated. For installations built or remodeled during 1933–1951, less than 2 per cent had no mix, 2 per cent had spiral flow, 6 per cent had baffles, 80 per cent used mechanical mixing, and 10 per cent employed other methods.

Today, nearly all plants provide mechanical mixing of one form or another.

CONDUIT MIXING BASINS

From the very beginning of the use of coagulation, it was realized that the chemicals should be uniformly distributed throughout the water to be treated, but it was thought that if sufficient time was available for the uniform distribution of the chemicals or if other means for the dispersal of chemicals were available, no further provisions for coagulation were necessary. Sometimes the coagulant was added to the water before it passed through the low-lift pumps, which probably produced a very rapid initial mixing, but no facilities were provided for flocculation. As it was noted that time was important, the raw-water conduits were sometimes used as mixing basins. The greatest trouble encountered in doing so lies in the length of conduit required for good coagulation. The coagulant must be added at a point sufficiently distant from the settling basins to permit some building up of the floc. Flocculation does occur in conduits with a straight-line flow, but in order to obtain the necessary turbulence for mixing, the velocity of flow must be high and the coagulation period must be long. At the St. Louis Chain of Rocks Plant, the velocity in the conduit is 3.3 fps at a flow of 150 mgd and the length of the conduit is 9,528 ft.

Other difficulties may be experienced in the use of pipelines or various closed conduits as mixing basins. Deposits from the chemicals may accumulate—especially when lime is added to the water—and may be difficult to remove. If chemicals are fed into lines under pressure, trouble may occur from air binding in the chemical lines. Usually, the provision of a long line merely to coagulate the water is not as economical as the conventional type of baffled basin or mechanical mixing basin. Where a line is necessary for transporting raw water and where it is convenient to have the chemicals applied at some distance from the settling basins, it may be reasonable to consider the use of the conduit as a mixing basin. The design should include facilities for cleaning and maintaining the conduit.

HORIZONTALLY BAFFLED MIXING BASINS

In the horizontally baffled mixing basin, the water travels back and forth around the ends of baffles, as illustrated in Fig. 1. The outside walls of this type of basin are usually constructed of reinforced concrete, with grooves for the insertion of wooden baffles, which, in most recent designs, are made adjustable so that velocities of agitation can be changed, if necessary.

Flows through many plants may vary from one-fourth of rated capacity to more than rated capacity. Therefore, there are considerable fluctuations in the velocity through the mixing basins. The violence of agitation depends upon the velocity through the basin, in turn affecting the efficiency of coagulation. The lack of control of this agitation probably constitutes the most serious objection to baffled basins or, for that matter, to any coagulation device whose efficiency depends on the rate of flow.

Because the optimum violence of agitation is a function of the characteris-

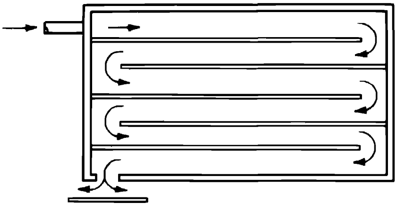

Fig. 1 Round-the-end baffled mixing basin. The water travels back and forth around the ends of the baffles.

tics of the water, the kind of chemical used, the chemical dosage, the temperature of the water, and the period of coagulation, determination of the velocity of flow is one of the most difficult problems in the design of a mixing basin. For instance, a velocity of 2.0 fps, although generally considered excessive, might be the most desirable one for coagulating a highly turbid water in a specific basin. Again, a velocity of 1.0 fps, though acceptable in the treatment of a number of slightly turbid waters, might result in the accumulation of sediment at the bottom of the basin if applied to highly turbid waters. When treating waters with such high solids loads, however, primary sedimentation may well be considered as a preferred method of preventing accumulation of sediment in mixing basins. The cost of installation may be partially offset by lower coagulant requirements.

In the absence of specific data, Baylis[5] has suggested that a velocity of about 1.3 fps for operation at rated capacity is probably the most desirable speed for highly turbid waters. On the same basis, he suggests a velocity of 0.8 fps for waters of low turbidity and a maximum of 1.0 fps for slightly turbid waters. Where the turbidity fluctuates from low to high, velocities may be related to the mean turbidity.

It is quite evident that, for the first few minutes when the coagulant is being dispersed, the velocities may be much greater without interfering with the final flocculation of the water. Also, it should be noted that there will be very localized, short-period, high velocities as the water passes around the ends of the baffles, with the eddies thus formed undoubtedly playing an important part in producing effective coagulation. The average loss of head appears to be between 2.0 and 3.5 times the velocity head for each 180° bend in the mixing basin.

VERTICALLY BAFFLED MIXING BASINS

Vertically baffled mixing basins are similar to the horizontally baffled type, except that in the latter, the water is directed vertically over and under a series of adjacent baffles, as shown in Fig. 2. Inasmuch as the direction of flow is the only significant difference between the two types of basins, their advantages and disadvantages are virtually the same. The alternate rise and fall of water obtained in the vertically baffled type is thought to be more effective in maintaining a homogeneous mixture of the suspended particles constituting the floc, thus preventing the undesirable deposition of sludge often encountered in horizontally baffled basins.

Little specific information is available on the best means of calculating the loss of head that will take place in horizontally and vertically baffled mixing basins. If the walls were perfectly smooth and straight, the friction loss could be computed with considerable accuracy by the use of hydraulic formulas, but this condition is not realized in practice. Furthermore, as the number of turns, supports, and bracing timbers varies considerably among different basins, even among those of the same general type, a coefficient determined for one might not be applicable to others. There is a much greater loss of head in a baffled mixing chamber than in those mechanically agitated, although with proper design the reduction may be kept at a minimum. An estimate of the head loss may be made by considering each lower pass as an orifice and each upper pass as a submerged weir.

MECHANICAL MIXING BASINS

Mechanical mixing basins are provided with mechanical devices designed to agitate the water to be treated at the most desirable degrees of violence. Agitators were used in water softening for some time before their applicability to coagulation was appreciated. After the value of a prolonged period of agitation had been established, however, the use of mechanical agitators —capable of providing both the violent turbulence required in the mixing period and the gentler agitation in the flocculation period—soon came to be accepted practice.

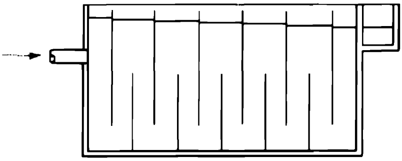

Fig. 2 Over-and-under baffled mixing chamber. The water is directed vertically over and under the adjacent baffles.

THEORY OF MIXING

Mixing is accomplished by the dissipation of power in the water. The concept of dissipating the power is important; simply adding energy to the water will not suffice. The rate of energy dissipation is closely related to the intensity of agitation or mixing accomplished in the water, and the intensity of agitation to be provided depends upon the purpose to be served by the mixing.

Rapid Mixing. Mixing for the rapid dispersion of chemicals and other materials throughout the water is best accomplished by generating intense turbulence in the water. In this turbulence, small-scale eddies form frequently and disappear rapidly. Their frequent formation and disappearance provides the means for rapid transportation of the added material to all parts of the water; and the small scale of the turbulence assures a uniformity of dispersion not accomplished with large-scale eddies which can transport large masses of water from one area to another without effecting substantial mixing. Through the years, many devices have been relied upon to provide the mixing needed for chemical dispersion: baffled chambers; hydraulic jumps; mixing chambers containing impeller or propeller mixers. As might be expected, these devices have not proven themselves to be equally effective. Generally speaking, the less effective devices are found wanting in one or more of the following key elements: high rate of power dissipation; small-scale turbulence; and flexibility of operation.

No clear-cut guidelines exist for determining the power dissipation or detention time required to disperse chemicals in the flow of water. However, detention times of 20 sec or less are not uncommon, and mixing units providing 1 to 2 hp for each cubic foot per second of flow rate are not unreasonable.[6]

A parameter frequently used to express the power input is the temporal mean velocity gradient G (which has the dimension of 1/time):

$$G = (P/\mu V)^{1/2} \qquad (1)$$

Here P is the power dissipated in the water (ft lb/sec); V is the volume of the tank or basin, or the volume of water to which the power is applied (cu ft), and μ is the absolute viscosity of the water (lb sec/sq ft).

Camp[7] studied the impact of rapid mixing on floc formation. He reported that mixing at G values of 500 sec^{-1} to 1,000 sec^{-1} for about 2 min produced essentially complete flocculation and that prolonged rapid mixing at this intensity accomplished practically nothing more. For rapid mixing with smaller G values, a 2-min period was insufficient to complete the flocculation; 5 min is a more appropriate time. However, mixing at excessively high G values (10,000 sec^{-1} or more) for as long a time as 2 min seemed to delay or retard floc formation substantially. Further studies on the role of rapid mixing in water processing are needed, particularly where precipitation and/or flocculation reactions are involved.

Flocculation. A theoretical basis for the influence of mixing on flocculation was first described by Smoluchowski[8] in 1918 and elaborated by Camp and Stein[9] in 1943. Specifically, the theory states that the rate at which particles of different size collide when subjected to mixing is proportional to: (1) the number of particles of each size; (2) the size of the particles; and (3) the local fluid velocity gradient in the suspension.

The fundamental equation may be written as:

$$N_{i_j} = \frac{1}{6} n_i n_j (d_i + d_j)^3 \frac{du}{dz} \tag{2}$$

Here N_{i_j} is the frequency of collision per unit volume of suspension between i particles and j particles, n_i and n_j are the numbers of i and j particles per unit volume of suspension, d_i and d_j are the respective particle diameters, and du/dz is the local fluid velocity gradient in the suspension. In a continuously flowing or mixed tank, the local velocity gradient is not constant, and so du/dz must be approximated by the temporal mean value G for the entire tank [see Eq. (1)]. A more detailed presentation of the theory of flocculation may be found in the paper by Camp and Stein[9] or the textbook by Fair, Geyer, and Okun.[10]

Examination of the flocculation equation indicates that the rate at which flocculation proceeds—that is, the rate of collision among particles—is strongly dependent upon (1) the number of particles present in the suspension (the number concentration), (2) the volume of the particles in the suspension (the floc volume concentration or volume fraction), and (3) the intensity of mixing in the flocculator (the temporal mean velocity gradient G). Since the flocculation equation depicts a rate process, the time provided for flocculation to occur must also be a significant factor.

Camp[11] analyzed the designs of several existing treatment plants and found that satisfactory performance of the flocculation process resulted when the mixing for flocculation provided values of G ranging from 20 sec^{-1} to 70 sec^{-1}. The detention times of the flocculation basins in these plants, when expressed in seconds and multiplied by the G value, yielded values ranging from 2×10^4 to 2×10^5. This product (GT) is nondimensional and has been considered by many to be a useful parameter for flocculator design and operation.

A similar dimensionless grouping of parameters arises from consideration of the flocculation theory. Multiplication of the product GT by the floc volume fraction C (volume of floc per unit volume of suspension) maintains the nondimensionality of the group while producing a new parameter GCT which reflects the contact opportunity afforded the particles in the flocculator.[12,13,14] In computer simulation studies, comparable floc growth rates and patterns were produced by comparable numerical values of this parameter. As yet an optimal value (or range of values) for the contact opportunity parameter has not been established, but data obtained from laboratory model studies by Harris, Kaufman, and Krone[13] suggest that the order of magnitude for the parameter may be about 100.[14] Such a value is consistent with the previously reported range for GT and a floc volume fraction ranging from 0.0004 to 0.001.[7]

Considerable evidence remains to suggest that the design and operation of flocculators may not be adequately represented by the parametric groups GT or GCT. Argaman and Kaufman[15] reported that flocculator performance is dependent upon both G and G^2 as well as T. Moreover, their studies indicate that the G value should be modified by a paddle coefficient and an energy-spectrum coefficient to account for the variety of turbulence conditions produced in the water by the different stirring mechanisms.

In laboratory studies on simulated natural waters, Gemmell and Fair[16] have shown that the removal of color and turbidity by flocculation is not adequately expressed by the parametric group GT. Figure 3*a* and *b* illustrate the residual dependence upon G obtained when the turbidity or color remaining is plotted against the GT value (logarithmic scales are used for both ordinate and abscissa).

Floc Properties. The flocs produced under different conditions of mixing have different physical properties. Many persons have reported that high paddle speeds or high G values cause flocs to break up.[11,17,18,19] Argaman and Kaufman,[15] Gemmell,[20] and Hudson[21] reported floc size to be inversely proportional to the G value although each used a different measure of size (diameter, projected area, and volume fraction, respectively). Experiments conducted by Lagvankar[22] indicate that the size (diameter) of the largest flocs in a suspension is inversely proportional to the G value at which the suspension was flocculated.

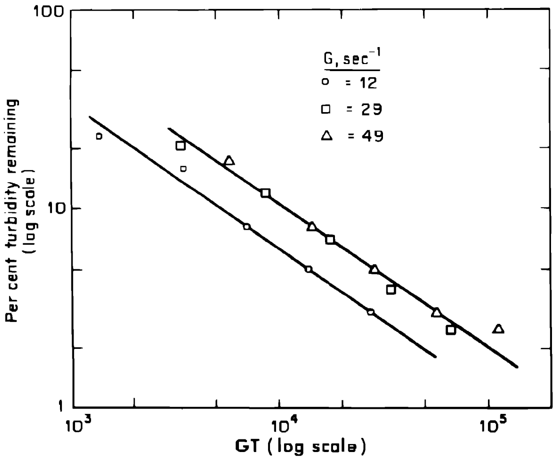

Fig. 3a Turbidity removal by coagulation. The reduction in turbidity is not adequately described by the mixing parameter GT.

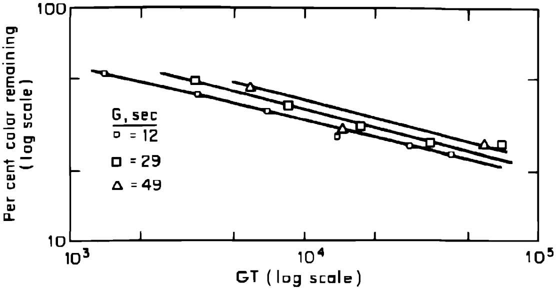

Fig. 3b Color removal by coagulation. The influence of mixing on color removal is not wholly described by the parameter *GT*.

The density of flocs has been shown to decrease with increasing floc size.[22,23] Figure 4*a* and *b* illustrate the form of the size-density variation. The change in slope of the curve which occurs at a floc size of about 1.5 mm^2 in projected area indicates a change in type or stage of aggregation. The slope of the size-density function pertaining to the flocs smaller than 1.5 mm^2 in projected area corresponds closely to that predicted by computer simulation studies.[24] Floc structure in this size range has been interpreted as a dense packing of primary flocs. The larger-size flocs, which show little variation in density with size, correspond to loose aggregations of flocs called floc aggregates. As the turbidity of the water increases, the density of the floc aggregates increases, and the size at which the transition from dense packing to loose aggregation occurs becomes smaller.

Hudson,[21] among others, suggested that floc density is dependent upon

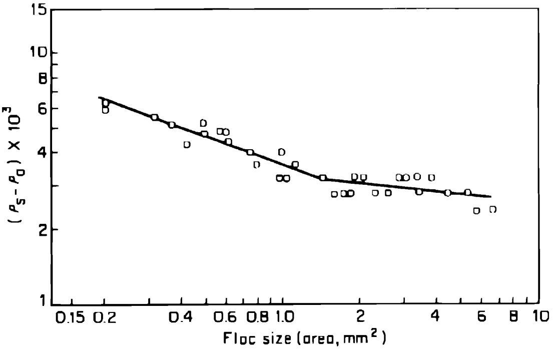

Fig. 4a Variation of floc density with floc size. Flocs generated with Fe$_2$(SO$_4$)$_3$ coagulant in absence of kaolin turbidity in high-alkalinity simulated natural water. Fe$_2$(SO$_4$)$_3$ = 1.6×10^{-4} mol/l; NaHCO$_3$ = 1×10^{-2} mol/l = 500 mg/l alkalinity as CaCO$_3$; G = 11 fps/ft; T = 30 min; pH = 6.8; temperature = 20°C; ρ_0 = 0.9991 g/cm^3. The type of floc aggregation encountered changes at about 1 mm diameter.

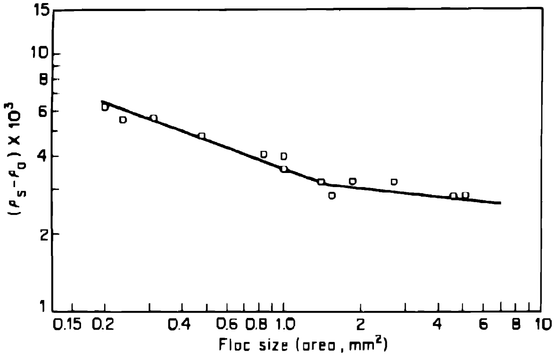

Fig. 4b Variation of floc density with floc size. Flocs generated with $Fe_2(SO_4)_3$ coagulant in absence of kaolin turbidity in low-alkalinity simulated water. $Fe_2(SO_4)_3 = 2 \times 10^{-5}$ mol/l; $NaHCO_3 = 2 \times 10^{-3}$ mol/l $= 100$ mg/l alkalinity as $CaCO_3$; $G = 11$ fps/ft; $T = 30$ min; pH $= 6.8$; temperature $= 20$ °C; $\rho_0 = 0.9985$ g/cm^3. The floc density relationships are not dependent on alkalinity.

the intensity of mixing provided in the flocculator, with higher densities resulting from more intense agitation (higher G). ‘It is generally true that floc suspensions subjected to higher G's exhibit an overall characteristic of higher density, but this is largely due to combined effects of the size-density variation just discussed and the fact that the higher G's inhibit growth (or breakup) of the larger flocs.’ Thus with more intense mixing, smaller flocs are produced which are inherently more dense. This interpretation is supported by the findings of Lagvankar and Gemmell,[23] who reported that flocs of the same size formed at different G's tend to have the same densities, as is shown in Fig. 5. According to Lagvankar,[22] fragments of flocs which have been purposely broken off a parent floc have a density corresponding to the size of the fragment rather than to the size of the parent floc.

Flocculation Time. The time provided for the flocculation process is of considerable importance. As was mentioned previously, flocculation time is one of the factors included in the contact opportunity parameter GCT. In theory, the longer the time provided, the more complete will be the flocculation. However, several factors acting in concert diminish the advantage of prolonged agitation. There is no doubt that extensive periods of flocculation enhance the probability of turbidity and other small particles being incorporated into the flocs, but most of this is accomplished in the first few minutes with only a small fraction remaining unflocculated. Thus, the bulk of the flocculation time is provided to condition the flocs for removal from the water by settling and/or filtration. Many researchers,[11,15,20,22] have shown that there is a flocculation time beyond which the largest flocs cease to grow and, indeed, disintegrate. No specific value for this time has been established, nor is it clear that such a time would be optimal for process performance.

Lagvankar[22] has shown that flocs actually become more dense, size-for-size, when flocculated for periods in excess of 30 min. However, approximately 6 hr of additional flocculation was required to double the buoyant density of the flocs. Generally, the saving in settling time which such a density increase would afford is not adequate to offset the additional flocculation time.

The complex manner in which flocculation performance depends upon flocculation time requires that provision be made to retain as much of the water as possible in the flocculation chamber for the period of time chosen. This can be accomplished by compartmentalizing the flocculation basin through the use of baffles. The effect of compartmentalization of a continuously flowing basin (of any type) is illustrated in Fig. 6.[8] As may be seen, a one-compartment basin permits about 40 per cent of the inflow to escape in less than half the theoretical detention time (equal to the tank volume divided by the flow rate through the tank) whereas a three-compartment basin reduces the amount to 20 per cent and a five-compartment basin, to about 10 per cent. Further increase in the number of compartments would continue the trend with the curve approaching a vertical line at the retention time-ratio of 1.0.

Design of Mixing Basins. The required degree of turbulence for rapid mixing is provided by a number of different mechanisms. The importance of flexibility in operation cannot be overstressed. Reliance upon conduit

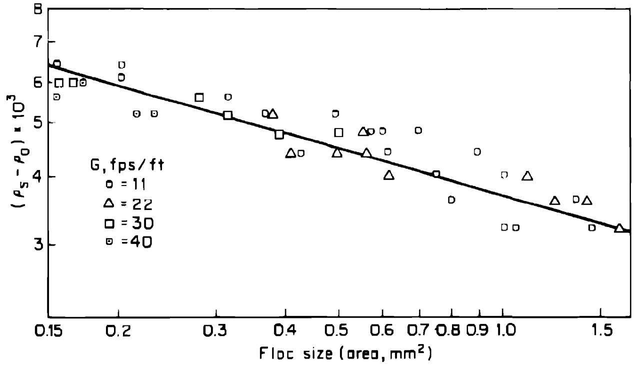

Fig. 5 Effect of velocity gradient on floc density. Flocs generated with $Fe_2(SO_4)_3$ coagulant in absence of kaolin turbidity in high-alkalinity simulated natural water. $Fe_2(SO_4)_3 = 1.6 \times 10^{-4}$ mol/l; $NaHCO_3 = 1 \times 10^{-2}$ mol/l $= 500$ mg/l alkalinity as $CaCO_3$; pH $= 6.8$; temperature $= 20\,^\circ C$; $T = 30$ min; $\rho_0 = 0.9991$ g/cm^3. The size-density relationship is essentially independent of the G value.

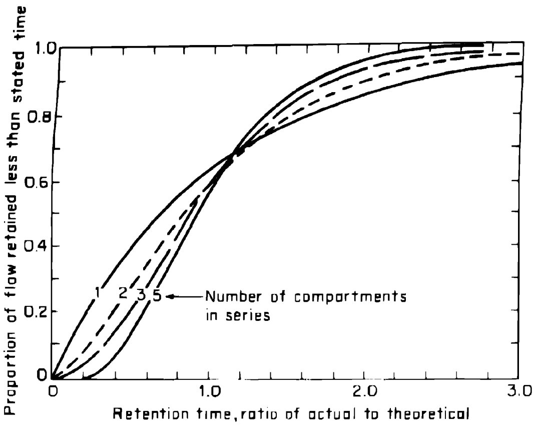

Fig. 6 Short circuiting in mixing compartments. A one-compartment mixing chamber permits approximately 40 per cent of the inflow to escape in less than half the nominal retention, while a five-compartment basin reduces this amount to about 10 per cent. The largest practicable number of compartments is, therefore, desirable.

flow, process pumps, baffled chambers, etc., to accomplish mixing leaves the plant operator with little or no opportunity to adjust the operation to suit the treatment needs. Instead, mixing conditions are determined by the rate at which the water is processed.

Because of their many desirable features, propeller, impeller, or turbine mixers have gained the widest acceptance in treatment-process design. These units are often placed in small chambers or tanks in which the agitation is well confined and the detention time short. In some instances, impeller or turbine mixers have been inserted in pipes or conduits, thereby eliminating the need for a separate tank or chamber. Three arrangements for rapid mixing are shown in Fig. 7*a*, *b*, and *c*.

The time required for flash mixing is short, ranging downward from 10 sec. The function of the flash mix is that of dispersing the coagulant through the water mass so that intimate and immediate contact is made. It is not desirable to cause formation of floc particles in flash mixers.

Equipment for floc formation should provide a gentler conditioning mix. One type of flocculation equipment, as illustrated in Fig. 8*a*, consists of a series of paddles placed transversely across the tank width. These are arranged to impart a barrel roll to the water.

There are usually two or more rows of paddles, with appropriate baffles between them to effect an additional up-and-down travel to the floc particles. The paddles are driven by a motor, either constant or multiple speed, mounted on the tank wall, with a chain or v-belt drive down to the shafts. It is advisable to install the drive elements in a dry well at the side or end of the tank and extend the ends of the shafts through the dry-well wall with bushings. Such installation permits constant inspection and lubrication of the chains and sprockets, avoiding the frequent replacement necessitated by corrosion and abrasion which could occur if the mechanism were submerged. Underwater bearings may be provided with automatic lubricators, filled with grease, which permit operation for a year or more without refilling.

Another widely used type of flocculating equipment consists of a central shaft installed longitudinally in the center of the basin, parallel to the

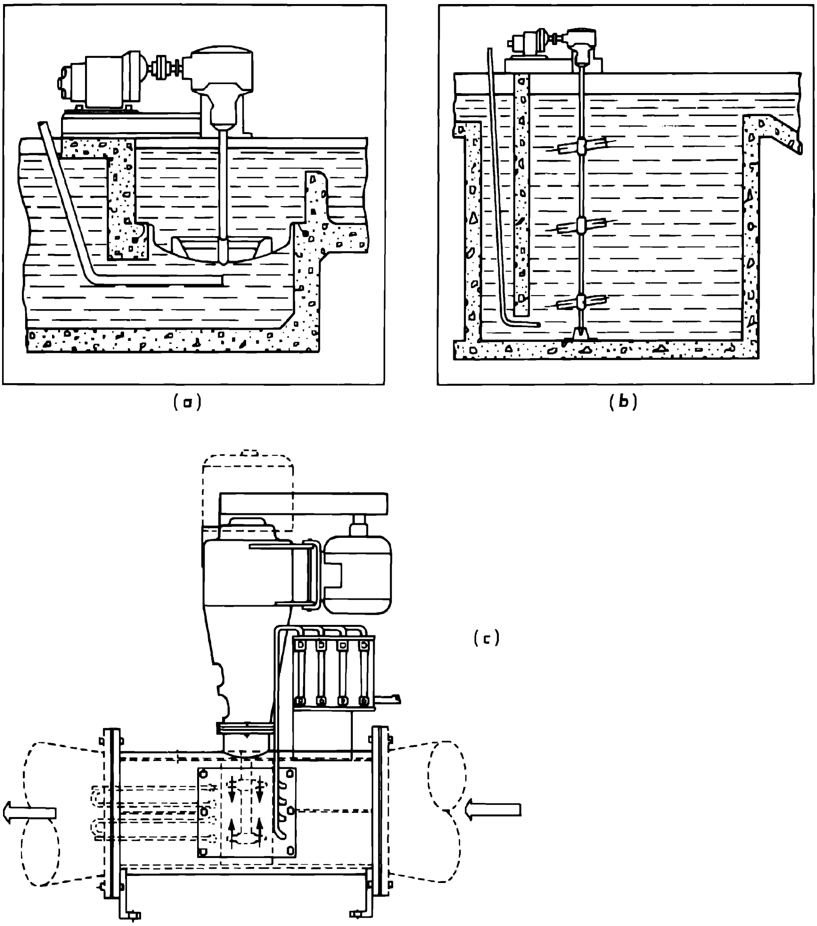

Fig. 7 Provision for rapid mixing of added chemicals may take many forms. *(a)* and *(b)* Mechanical mixing tanks for chemicals. *(c)* An in-line mixer for chemicals.

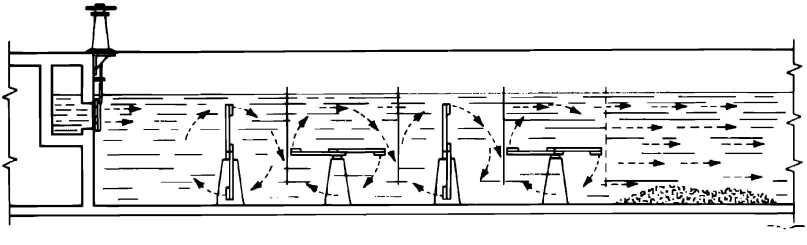

Fig. 8a Flocculating equipment. A series of paddles placed transversely across the tank width are arranged to impart a barrel-roll motion to the water.

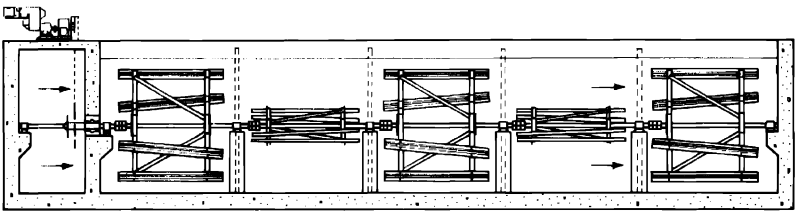

Fig. 8b Paddle reel flocculator. The intensity of mixing depends on the area of the paddle blades and the rotational speed of the shaft. The water flows in the direction of the drive shaft.

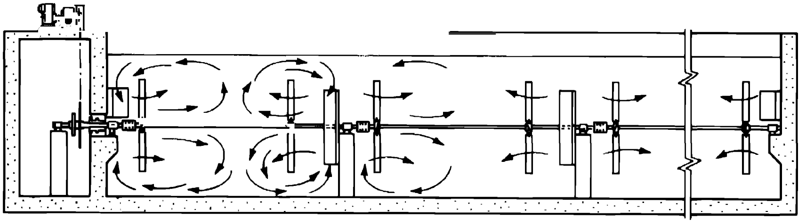

Fig. 8c Axial-flow propeller flocculator. This mixing unit is similar to the paddle reel flocculator.

direction of flow; attached paddles rotate about the central shaft in a direction perpendicular to the flow. See Fig. 8*b*. These models are usually designed with the paddle area decreasing in the direction of the flow to provide for diminishing agitation as the water progresses through the basin, while baffling is required at intervals to prevent the water from "coring" through the center of the basin along the shaft in the area of minimum turbulence. These units are usually equipped with variable speed drives. An advantage of the longitudinal shaft is that it can be driven through a stuffing box at one end of the basin, obviating a dry well for the drive chain. Figure 8*c* shows a variant of this flocculator arrangement in which propellers are used in place of paddles.

Another mixer for floc conditioning is shown in Fig. 8*d*. This type, which has variable speed drive and is readily adaptable to existing basins, is described in a 1944 *J. AWWA* article.[25]

The vertical axial-flow flocculator relies upon a relatively small, high-speed impeller to impart the mixing and turbulence needed to promote flocculation. As may be seen from Fig. 8*e*, the installation is simple and easy to maintain, and the arrangement is readily adapted for use in circular tanks.

Mixing basin designs and material of construction should be determined after an engineering investigation of the particular plant requirements. Mixing basins have been constructed of both steel and concrete and in various shapes, such as square, oblong, or circular. Practice has shown that, normally, a flocculation period of from 30 to 45 min—depending upon the character of the water—is required for good results.

The principal advantage of the mechanical mixing basin over other types is that mechanical mixing permits the maintenance of certain states of motion irrespective of rates of pumpage or filtration as well as making readily possible the adjustment of flocculation velocity to suit changing conditions.

OTHER TYPES OF MIXING

Occasionally, unusual types of mixing basins or agitation devices are used in an effort to improve plant results. Prominent among these innovations are the hydraulic-jump method of agitation and the application of various aeration devices to aid coagulation.

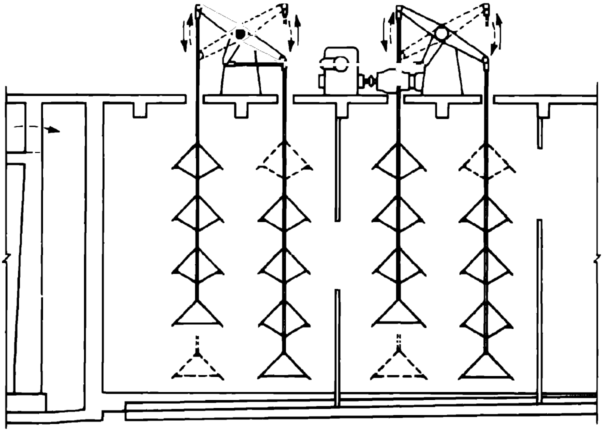

Fig. 8*d* Walking beam flocculator. The up-and-down motion of the paddles provides gentle agitation.

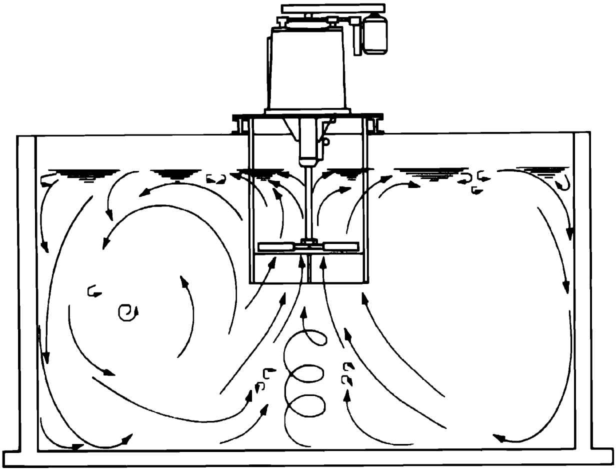

Fig. 8e Turbine flocculator. This device is easy to install in existing basins.

The hydraulic jump is essentially a method of providing a rapid mix without the use of mechanical units. Coagulant is introduced into the water before it enters an open, sloping, and widening flume. Passing down the flume, the water acquires a high velocity, 10 to 12 fps. On reaching the bottom, the water enters a slowly moving pool. Here, some of the kinetic energy acquired in flowing down the flume is dissipated, resulting in considerable turbulence, which, in turn, ensures a rapid initial mix. The head loss is at least 1 ft.

Aerating devices have been used for mixing and flocculation. Where such agitation is applied properly, it will produce very satisfactory results. It is doubtful, however, whether it has any advantage over the conventional mechanical agitators.

SEDIMENTATION

Sedimentation is the separation of suspended solids from water by gravity. The solids may be in their naturally occurring form, such as silt or similar material, or in a form modified from their original state, as by coagulation or chemical precipitation. Whatever their origin, the particles, if more dense than water, settle, and whenever they leave the stream of flow, generally by striking the bottom of the tank or basin, they are considered removed from the water. Particles less dense than water tend to rise, and if provision is made for their collection or retention in the basin, they are similarly considered removed from the water. Thus the clarification of water by sedimentation or settling is a natural process, and evidence of its purposeful utilization reaches us from antiquity.[1]

In ancient Egypt, the turbid floodwaters of the Nile were diverted to stilling basins and allowed to settle before distribution for domestic use. In the ruins of Carthage, the remains of large rainwater storage and settling reservoirs, erected for public supply, have been found. In Rome, settling reservoirs for improvement of water quality were built before the Christian era.

SEDIMENTATION THEORY

Basically, the theory of sedimentation is the theory of the effect of gravity on particles suspended in a liquid of lesser density. Under the influence of gravity, any particle having a density greater than 1.0 will settle in water at an accelerating velocity until the resistance of the liquid equals the effective weight of the particle. Thereafter the settling velocity will be essentially constant and will depend upon the size, shape, and density of the particle, as well as the density and viscosity of the water. For most theoretical and practical computations of settling velocities in sedimentation basins, the shape of the particles is assumed to be spherical. Settling velocities of particles of other shapes can be analyzed in relation to spheres.

The general equation for the settling velocity of spheres is

$$V = \left[\frac{4g(\rho_s - \rho)d}{3C_D\rho} \right]^{1/2} \tag{3}$$

where V is the settling velocity of the particle, g is the gravity constant, ρ_s is the density of the particle, ρ is the density of the water, d is the diameter of the particle, and C_D is a drag coefficient. The drag coefficient is not constant but is dependent upon the Reynolds number

$$R = \frac{Vd\rho}{\mu} \tag{4}$$

where μ is the absolute viscosity of the water and V, d, and ρ are as stated before.

The value of the drag coefficient is approximated by the following equation:

$$C_D = \frac{24}{R} + \frac{3}{R^{1/2}} + 0.34 \tag{5}$$

For low Reynolds numbers ($R < 0.5$), $C_D = 24/R$ and when this relationship is inserted in Eq. (3), it becomes

$$V = \frac{g(\rho_s - \rho)d^2}{18\mu} \tag{6}$$

which is known as Stokes law. For high Reynolds numbers ($R > 10^3$), the drag coefficient is nearly constant at a value of about 0.4. Shapes other than spheres show a similarly constant, but higher, drag coefficient at high Reynolds numbers. The settling velocities of nonspherical particles may be calculated by evaluating an equivalent spherical diameter and a shape coefficient for the particle.

Particles which settle at velocities in accordance with the equations given previously are said to behave as discrete particles in that their settling is not influenced by the presence of other particles. More will be said about particle interaction later. However, for discrete settling of particles, a rational theory for predicting the removal of suspended matter was developed by Camp.[19]

Ideal Settling. The general form of an ideal basin is illustrated in Fig. 9. A unit of water entering the ideal sedimentation basin at the left is assumed to spread out uniformly over a vertical plane A-A in such a manner that the concentration of suspended particles of all sizes and densities is constant throughout an incremental volume of the tank, which has a length of ΔL. The portion of the basin where this process takes place is called the inlet zone. The incremental volume of water moves from inlet to outlet, through the settling zone, at a uniform velocity v and arrives at the position A'-A' without change in shape. The velocity v is equal to the flow rate Q divided by the cross-sectional area of the basin h_0W, where h_0 is the depth and W is the width. In the outlet zone, increments of water reassemble from all parts of the plane A'-A' to reconstitute the original unit of water, carrying along all the particles which are not removed in the settling zone.

Assuming that all particles settle discretely and that those which strike the bottom are removed, the absolute velocity path V represents the maximum elevation where particles of the smallest settling velocity V_0 which will experience 100 per cent removal may be found. That is, a particle with settling velocity V_0 which enters the basin at the water surface (at height h_0 above the bottom) will travel along the path V and be removed just as the water moving at velocity V enters the outlet zone. All other

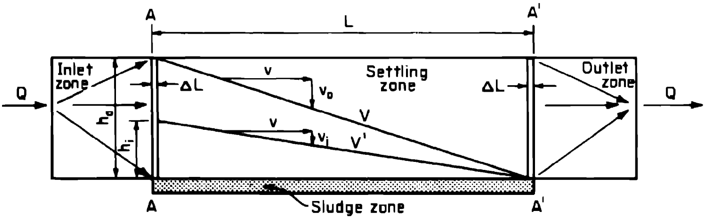

Fig. 9 Ideal sedimentation basin. For an explanation of symbols employed, see text.

particles of the same settling velocity will follow parallel paths and be removed nearer the inlet end of the basin. The settling velocity (V_0) of the particle will, of course, be governed by its diameter and density in accordance with the appropriate equation.

Particles with settling velocities V_i less than V_0 will follow an absolute path parallel to V'. Consequently, they will be carried over the outlet if they originate above h_i in the plane A'-A' or be removed if they enter the tank at a lower elevation.

The time t available for a particle to settle is $t = L/V$, and so the critical settling velocity V_0 is $V_0 = h_0/t$. As was stated earlier, $v = Q/h_0W$ and the combination of this relationship with the previous two yields

$$V_0 = \frac{h_0 W}{L} = \frac{h_0 Q}{h_0 WL} = \frac{Q}{WL}$$

The quantity WL is the surface (bottom) area A of the basin, and

$$V_0 = \frac{Q}{A} \tag{7}$$

The quantity Q/A, known as the surface loading or overflow rate, identifies the smallest settling velocity attributable to the class of particles which experiences complete removal from the water in passing through the settling zone. Notice that it is independent of the depth of the basin. Because

$$\frac{V_0}{V_i} = \frac{h_0}{h_i}$$

the percentage removal experienced by a class of particles with settling velocities V_i smaller than V_0 will equal 100 V_i/V_0. For any suspension, then, if p_i is the proportion of particles having settling velocities less than or equal to V_i the total proportion p of particles which could be removed in settling would be

$$P = (1 - p_0) + \int_0^{p_0} \frac{v_i}{v_0}\, dp_i \tag{8}$$

These relationships are illustrated in Fig. 10a, b, and c.[26] Figure 10a depicts two forms for displaying the settling velocity characteristics of a suspension: the cumulative curve (left ordinate), which expresses the proportion of material settling at velocities less than or equal to the indicated value; and the distributive curve (right ordinate), which is the derivative of the cumulative curve and expresses the incremental concentration (per 0.01 cm/sec increment) settling at the velocity shown. Calculation of the total quantity of material removed in passing through an ideal settling basin is best accomplished with the aid of the cumulative curve and Eq. (8) as shown in Fig. 10b.

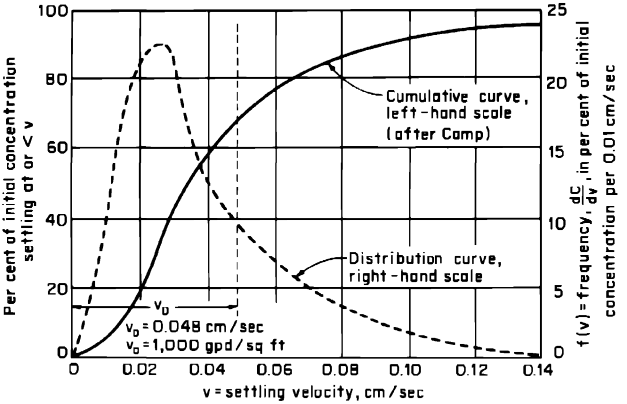

Fig. 10a Settling velocity functions for a typical suspension.

The relationship of influent suspension characteristics to the effluent suspension characteristics is depicted in Fig. 10c. Notice that the change in the quantity of suspension having a particular settling velocity V is a/b, which in turn is equal to the ratio of that settling velocity to the surface loading V/V_0.

The theory of ideal settling, presented here in the context of a rectangular basin, holds equally well for circular basins in which the flow is radially outward with a centrally located inlet zone and a peripheral outlet zone. In this case, the particle trajectories V and V', shown in Fig. 9 as linear for a rectangular basin, curve downward as flow progresses outward (from

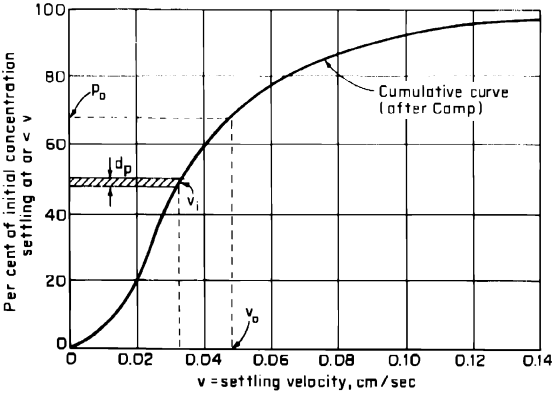

Fig. 10b Definition sketch for calculating total removals in ideal settling.

inlet to outlet zone). The incremental increase in surface area as the flow progresses outward just offsets the change in horizontal flow velocity which causes the downward curvature, so that the settling performance remains dependent only upon the surface loading Q/A. Neither basin depth nor detention time is important according to this theory.

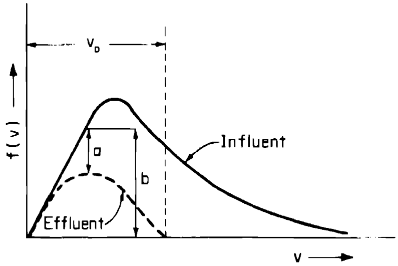

Fig. 10c Sample influent and effluent suspension relationship for an ideal tank.

Departure from Ideality. Unfortunately, settling basins seldom perform in accordance with ideal settling theory. Two factors are predominant in the departure of basin performance from ideality: currents and particle interactions. Several types of currents may be identified, the most common being: surface currents, induced by the wind blowing over uncovered basins; convection currents, arising from temperature differences within or around the basin; density currents, wherein the inflowing water is of a different density (due to temperature or the suspension load) from the water already in the basin; and eddy currents, produced by the inertia of the incoming water. These currents transport suspended matter to various parts of the basin (vertically and horizontally) and thereby distort the flow pattern from that assumed under ideal conditions.

Currents. Disregarding for the moment the influence of particle interactions, the effect of currents is to reduce the performance of the basin from that predicted by ideal theory. One approach for estimating the effect of currents is that devised by Hazen[27] and elaborated by Fair.[28] By assuming that the currents produce mixing in the basin not unlike the mixing basins in series described earlier in this chapter, Hazen estimated the settling performance which would result if a settling basin were subdivided into a sequence of mixed basins. In accordance with Fig. 6, a larger proportion of the flow is retained in the settling basin for the desired time (theoretical detention time) when the basin is subdivided into a large number of sequential units. If y_0 is the initial quantity of particles in a suspension possessing a settling velocity of v, the quantity of such particles which will be removed in the basin is y, and the proportion removed is

$$\frac{y}{y_0} = 1 - \left[1 + \frac{V_0}{n(Q/A)}\right]^{-n} \tag{9}$$

where n is the number of (hypothetical) basins in series and Q/A is the surface loading. Basin performance curves determined by Eq. (9) are presented in Fig. 11 for several values of n. Notice that for $n = 1$ in Hazen's theory, only 50 per cent of the particles with settling velocity V_0 (equal to the surface loading Q/A) will be removed, whereas 100 per cent of such particles would be removed in accordance with ideal theory.

If the settling velocity distribution is known for a suspension influent to a sedimentation basin, the settling velocity distribution for particles in the effluent may be estimated by application of either the ideal or the Hazen theory. The relationship of basin performances predicted by these theories is illustrated in Fig. 12 for a basin with a surface loading Q/A of 1,000 gpd/sq ft ($V_0 = 0.048$ cm/sec). The ordinate is the fraction of the *initial* suspension concentration (per 0.01 cm/sec settling velocity increment) possessing settling velocities indicated on the abscissa. This ordinate is the same one used for the distributive curves of Fig. 10*a* and *b*, and the upper curve of Fig. 12, designated influent, is the same curve shown on these earlier figures. The ordinate value associated with the effluent suspension curves represents the amount of the material in the initial suspension

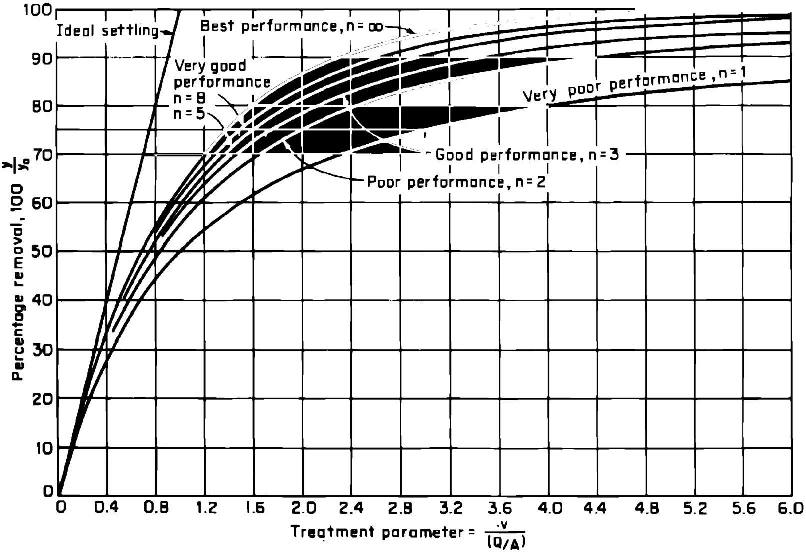

Fig. 11 Performance curves for settling basins of varying effectiveness. *(After Fair.)*

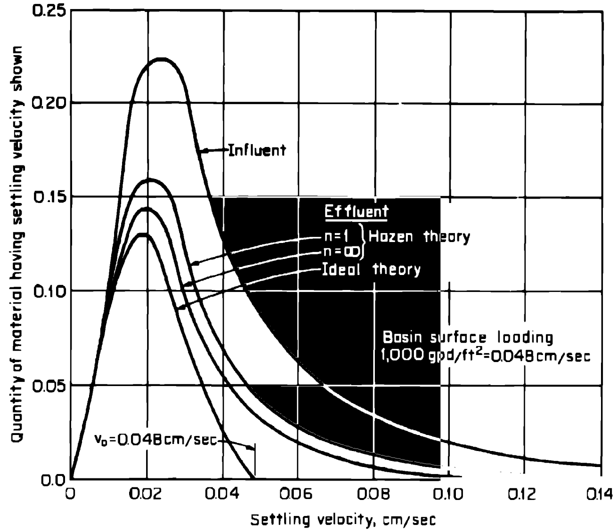

Fig. 12 Influent and effluent suspension settling velocity distributions according to ideal theory and Hazen's theory ($n = 1$ and $n = \infty$).

which remains in the effluent. Thus, the portion of the influent suspension which is removed in passing through the basin is indicated by the area between the influent curve and the appropriate effluent curve. Notice that the Hazen theory predicts poorer removals at all settling velocities and that at no settling velocity is complete removal of particles achieved, although for all practical purposes the quantity of material not removed becomes vanishingly small at high settling velocities.

Since a sizable amount of the suspension has settling velocities smaller than the overflow rate V_0 (surface loading), performance of the basin is not especially good. For this influent suspension, a smaller surface loading would increase removals in the basin substantially. Figure 13 shows the effect of passing the same influent suspension through a basin operated at half the surface loading ($Q/A = 500$ gpd/sq ft or $V_0 = 0.024$ cm/sec) as was used for Fig. 12.

Evaluation of the basin performance characteristic n in the Hazen equation should be based on experience with that or similar basins but may be estimated from tracer studies of the basin. In accordance with the assumption of mixed basins in series, the number of such (hypothetical) basins may be determined by placing a quantity of dye or other tracer material (such as salt) in the influent to the basin and observing the concentration of tracer in the basin effluent as time progresses. The value of n may be calculated using the relationship

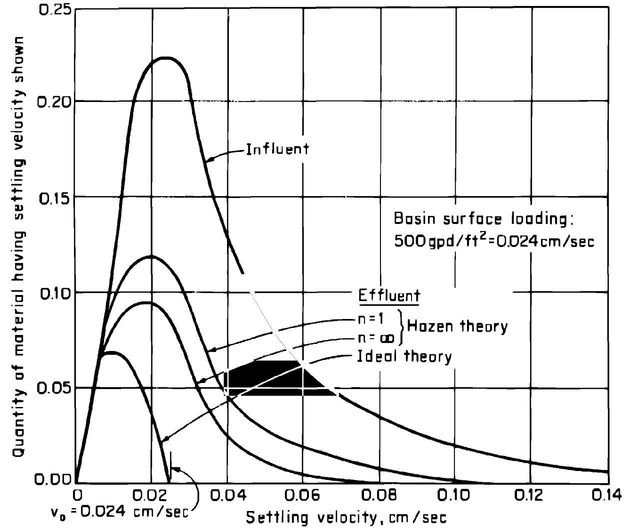

Fig. 13 Influent and effluent suspension settling velocity distributions according to ideal theory and Hazen's theory ($n = 1$ and $n = \infty$).

$$n = \frac{t_{\text{mean}}}{t_{\text{mean}} - t_{\text{mode}}} \tag{10}$$

where t_{mean} is the mean time required for the tracer to flow through the basin and t_{mode} is the time required for the highest concentration to appear in the effluent. These times are identified on the typical tracer curve shown in Fig. 13. In most instances, the mean retention time is equal to the theoretical detention time T (equal to the basin volume divided by the flow rate), with any discrepancies between an observed mean time and the calculated theoretical value arising from errors in the observed value. These errors may be due to inadequate instrument sensitivity when determining the concentration of tracer in the effluent or to adsorption (and subsequent desorption) of the tracer on the basin walls or to both. Furthermore, use of the theoretical detention time in place of the mean detention time simplifies the experimental procedure since tracer concentration measurements in the effluent need be continued only until the results assure that the peak concentration has passed. Instrument calibration is also less critical since only the time of appearance of the maximum concentration is needed and not the concentration itself.

Currents or high flow velocities near the bottom of the basin may cause particles which had previously reached the bottom or entered the sludge zone to become resuspended. This action is known as scour, especially when high flow velocities are the cause. The flow velocity at which this process begins is known as the scour velocity; its value depends upon the nature of the settled material. In many cases the particles so affected are not lifted great distances but are transported along the bottom toward the outlet zone, being lifted and dropped many times. Avoidance of scour is a significant factor in determining minimum basin depths for, at a constant surface loading, the average flow velocity of a basin is inversely proportional to the depth. As a consequence, depths less than 8 ft are rarely encountered except under special circumstances.

Currents generally can be reduced to acceptably small values by proper basin design. Covers for basins eliminate wind-induced currents and reduce the likelihood of rapid or severe temperature variations which produce convection currents. Baffle walls placed at the inlet and sometimes the outlet ends of the basin reduce inertial currents and aid in distributing the flow uniformly across the basin, thereby diminishing the likelihood for density currents to form.

Particle Interactions. Particle interactions manifest themselves in three ways, one of which accelerates settling whereas the others retard it. Settling is accelerated by the occurrence of flocculation within the sedimentation basin itself. Since different particles in a suspension may settle at different rates, one particle may overtake another as both settle, and, if they touch and stick together, flocculation occurs. The larger particle so formed generally settles at a higher velocity than either of the two separately. A floc may contact many other flocs in the course of settling, each time adding to its size and settling velocity. An equation expressing

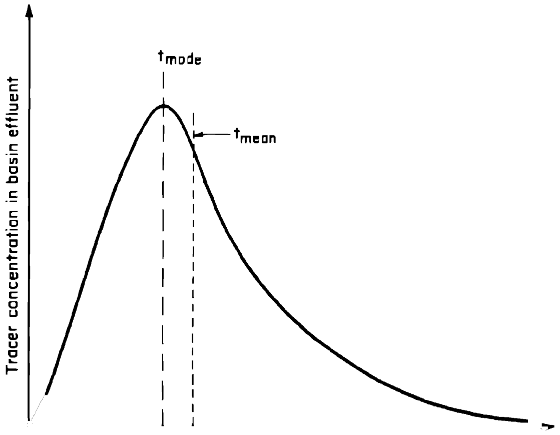

Fig. 14 Time after addition of tracer to basin influent.

the contact opportunity was devised by Camp.[9] It resembles the flocculation equation presented earlier [Eq. (2)] with the replacement of the velocity gradient term by a difference in settling velocities.

$$N_{i_j} = n_i n_j \frac{\pi}{4} (d_i + d_j)^2 (v_i - v_j) \tag{11}$$

As before, N_{i_j} is the frequency of collision per unit of volume of suspension between i particles and j particles, n_i and n_j are the numbers of i and j particles per unit volume of suspension, d_i and d_j are the respective particle diameters, and v_i and v_j, their settling velocities.

In addition to this mechanism, velocity gradients due to the flow and to currents in the sedimentation basin may promote flocculation as described in the section on mixing presented earlier. In accordance with Eqs. (3) and (6), settling velocities increase with increasing particle size, assuming that all other factors remain constant.

Chemical flocs of the kind formed in water treatment have been shown[22,23] to have densities which decrease with increasing floc size. The rate of decrease is more pronounced for small flocs (less than about 1 mm in diameter) than for large ones. Figure 4*a* and *b* depict the relationships for iron flocs in low-turbidity water. The density variation for small flocs as shown in these figures may be represented by the equation

$$\rho_s - \rho_0 = kd^{\;0.7} \tag{12}$$

where ρ_s is the density of the floc, ρ_0 is the density of the water (hence $\rho_s - \rho_0$ is the buoyant density of the floc), d is the equivalent spherical diameter of the floc, and k is a coefficient which depends upon the coagulant(s) used, the nature and amount of the turbidity, and other raw-water characteristics. Substitution of Eq. (12) in Eqs. (3) and (6) demonstrates that the settling velocity still increases with increasing floc size, but to a reduced extent. At low Reynolds numbers, the settling velocity increases in proportion to $d^{1.3}$, whereas at high Reynolds numbers, the increase is proportional to $d^{0.15}$. As was stated earlier in this chapter, the amount of turbidity present in the water and the flocculation time provided alter the floc size at which the type of aggregation (and hence the size-density variation) shifts from one form to another. The effects of the size-density variations encountered in actual plant operation may well be less extreme than those described here. Nonetheless, the conditions reported here may be considered limiting conditions, and the implications go beyond settling to filtration performance as well.

In addition to flocculation, particle interactions may produce an effect known as hindered settling. The equations [(3) and (6)] for calculating the settling velocity of a particle assume, among other things, that the particle is settling alone in quiet water. Since a particle displaces water below it as it settles, the water so displaced must move upward past the particle. For a single particle settling in a large vessel the upward movement of the displaced water goes virtually unnoticed; but if the concentration of particles is sufficiently great (or if the vessel is small in diameter relative to the size of the particle), the upward velocity of the water displaced by the particles becomes sizable in comparison with the settling velocity. Since the calculated settling velocity is relative to the water, the upward flow of displaced water acts to reduce the velocity at which the particle approaches the bottom of the basin. (Hindered settling is akin to the fluidization or expansion of a sand bed during backwashing.) The simplest and most widely used equation for estimating the extent to which settling is hindered is that devised by Richardson and Zaki.[29]

$$\frac{v_h}{v} = (1 - C_v)^n \tag{13}$$

where v_h is the hindered settling velocity, v is the unhindered settling velocity [as calculated by Eq. (3) or (6)], C_v is the volumetric concentration of particles in the suspension (volume fraction), and n is an exponent which, for spheres settling at Reynolds numbers less than 0.2, has a value of 4.65.

In a sedimentation basin, the volumetric concentration of particles tends to increase toward the bottom with an attendant increase in hindering. Since hindering reduces the effective settling velocity, it acts counter to the effects of flocculation. However, in most flocculators the floc volume fraction is less than 0.001. A tenfold increase in this value during settling would produce a decrease in particle settling velocity of less than 5 per cent, an amount wholly negligible in comparison to other effects on settling. Thus for a typical settling basin used in water treatment, the effects of hindered settling may be neglected. For some special situations or particular types of units used in water treatment (discussed later in this chapter), the particle volume fraction may be quite large, and when such conditions are encountered, consideration must be given to the effects of hindering.

EXPERIMENTAL WORK

Mixing and settling exhibit certain characteristics which are general to all waters. Because the latter are dissimilar, however, continuous experimentation is necessary for new plant design, development of coagulation theory, and improvement of plant operation. Experimental data may be obtained from models, pilot plants, laboratories, and operating installations.

Models for hydraulic design require both geometric and dynamic similarity, a condition which can be achieved. However, such models are not satisfactory for floc-settling studies because there is no practical way of scaling down the particles to be settled.

Laboratory experiments—usually specific for a particular water—are used both for plant design and for the improvement of plant performance. Experiments for plant design include studies on comparative efficiencies of available coagulants, dosages, rates of agitation, and sedimentation rates.

NUMBER OF BASINS

Probably the most important considerations in the selection of the number of basins are: (1) the effect upon the production of water if one basin is removed from service and (2) the largest size which can be expected to produce satisfactory results. Plant layout and site conditions also may influence the number of basins.

If there is only a single basin, its removal from service may make the consumption of raw water necessary. For any supply which requires coagulation and filtration for the production of safe water, a minimum of two basins should be provided. The greater the number available, the less will be the effect upon velocity and detention period in the remaining basins should one be out of service for cleaning, repairs, or any other reason.

SIZE AND SHAPE OF BASINS

The most common forms of sedimentation basins are circular, square, or rectangular. The selection of the particular form or shape for a given plant depends upon area available, conformity with adjacent structures, and the theories and experience of the designing engineer. The majority of sedimentation basins now in use are rectangular in shape and of reinforced concrete construction. Circular basins of either concrete or steel have been used widely for both coagulation and softening.

Most sedimentation basins are provided with sloping bottoms to facilitate the removal of deposited sludge. Although the optimum depth of a basin is a controversial matter, a review of the design of the larger rapid-sand filtration plants indicates a range of 8 to 16 ft in depth.

Multiple-story basins, in which the water travels horizontally along one level of a basin and then passes vertically (preferably upward) to another level of the basin for more horizontal flow, have been used successfully to compress a large amount of basin surface (bottom) area into a small area of the plant site. In this way low values of the surface-loading parameter can be attained, producing high removal efficiencies. Figure 15 shows a sectional view of a two-story tank. Since long, narrow tanks tend to have better hydraulic stability characteristics (less tendency to short-circuit) than short, wide ones, some designers place the several stories or levels in series rather than parallel. Although the same value for the surface-loading parameter can be attained with either flow arrangement, the parallel arrangement avoids the upsets caused by series arrangements in the area where flow direction reverses.

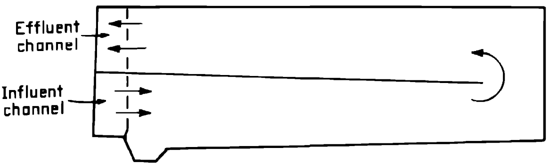

Fig. 15 Two-story sedimentation basin.

A recent innovation, the "tube" settler, uses parallel flow upwards through tubes about 2 in. square inclined at an angle of 60° from the horizontal to attain extremely high surface areas.[30] The tubes are short (2 to 4 ft) and the detention time for water in the "settler" is between 3 and 6 min. The 60° angle inclination permits accumulated sludge to slide down the tube wall to a sludge collector area. An alternate design uses 1-in. hexagonal tubes inclined at 5° from the horizontal. In this case, the tube settler requires separate provision for sludge removal, commonly by backwashing with filter washwater. The two arrangements are shown in Fig. 16. The steeply inclined tubes are constructed of plastic in modules which can be readily installed in existing sedimentation basins. Experimental work is in progress on plate settlers using asbestos-cement sheets instead of tubes.

INLET ARRANGEMENT

The purpose of inlets is to distribute the coagulated water uniformly among the basins and uniformly over the cross section of each sedimentation basin. Properly designed inlets and outlets are necessary to avoid short-circuiting through a basin. The most efficient and satisfactory inlet is one which permits water from the coagulation basin to enter directly into the sedimentation basin without the use of pipelines or flumes. As treatment plants operate over a relatively wide range of flow—from low winter to maximum summer demands—velocities occurring in the inlet pipeline or flume may be either so low that settling takes place or so high that the floc is broken before it reaches the basin. The permissible velocity range for any water and floc can be determined by tests, but velocities between 0.5 and 2 fps are usually satisfactory.

Where inlet pipelines or flumes are required, several methods have been used to give uniform distribution of the floc, as shown in Fig. 17.

To obtain uniform flow through each of the inlet pipes or orifices, the head loss at each opening should be large compared to the maximum difference of energy head available at the inlets. Velocities, however, must be maintained sufficiently low to prevent breaking up of floc.

INTERMEDIATE

The use of baffles in sedimentation basins to reduce short-circuiting and improve settling efficiency is common to many plants. Although such an arrangement does tend to correct short-circuiting, it may form dead spaces, produce eddy currents, and cause disturbance of the deposited solids. Another expedient for reducing short-circuiting is the use of longitudinal round-the-end baffles, which also serve the purpose of bringing water in at one end of the basin and returning it to that end before it goes on to the next step in the treatment process. Intermediate baffling has been less popular in recent years because of increased costs of construction and the use of mechanical mixing and flocculation to produce a floc having superior settling characteristics.

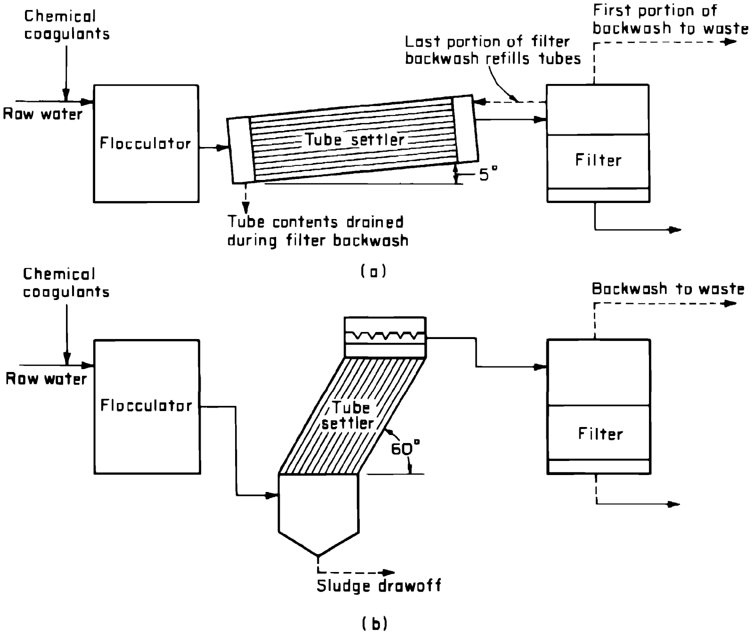

Fig. 16 Basic tube-settler configurations. *(a)* Essentially horizontal. *(b)* Steeply inclined. *(After Culp.)*

OUTLET ARRANGEMENTS

Water leaving the sedimentation basin should be collected uniformly across the width of the basin to prevent high velocities of approach and consequent lifting of the settled sludge over the weir.

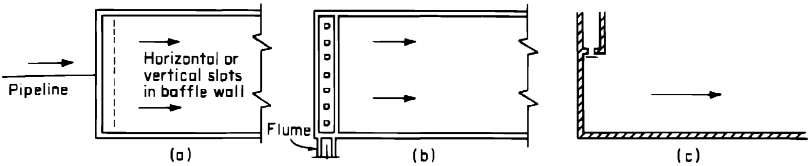

Fig. 17 Inlet arrangements. *(a)* Plan view of basin with pipeline inlet. *(b)* Plan view of basin with flume inlet. *(c)* Section view of *(b)*.

In rectangular basins, weirs may be constructed across the basin, or slots or effluent ports provided. Freely discharging weirs have a tendency to break fragile floc. Combinations of effluent orifices ahead of the submerged weir provide efficient outlet arrangements and reduce short-circuiting. In some designs, collecting weirs and flumes which begin at the middle of the basin to give great weir length have been constructed. Insufficient length results in excessive overflow rates and consequent high velocity of approach to the weir. Frequently, in basins of insufficient weir length, settled solids are pulled from the floor of the basin by high velocity of approach, nullifying the good settling which had been achieved.

DETENTION TIME

The time theoretically required for a unit volume of water to flow through a mixing or sedimentation basin is called the "detention time." It is equal to the time required to fill the basin at a given rate of flow and can be computed by dividing the volume of the basin by the rate of flow through it.

Detention time must be distinguished from the "flowing-through time," the minimum time required for a particle of water to pass through the basin. The detention period may vary from nearly one to twenty times the flowing-through period, depending upon the shape and dimensions of the basin, the design of the inlet and outlet structures and baffles, and other factors which affect the degree of short-circuiting that occurs in the basin. A method for evaluating the detention characteristics of basins was presented in the section describing the effects of currents on settling.

The desirable detention time is affected by the purpose of the basin. In a mechanically cleaned presedimentation basin, the detention time may be sufficient for the removal of only the coarse, rapid-setting sand

and silt. In a plain sedimentation basin, depended upon for removal of fine suspended solids, the detention time must be long—in fact, the longer the better—as small particles settle very slowly.

In a properly designed settling basin which handles well-coagulated water, a detention time of from 2 to 4 hr is usually ample to prepare the water for filtration. When economy is not a governing factor or where a high degree of suspended-solids removal is desired, the settling basins may be somewhat larger than required for minimum detention.

VELOCITY OF FLOW THROUGH SEDIMENTATION BASINS

A survey of 60 large rapid-sand filtration plants shows that theoretical velocities vary from a minimum of 0.5 to a maximum of 5.7 fpm, averaging 1.9 fpm. The velocity in a sedimentation basin, however, is not uniform over the cross section, even though the inlet and outlet arrangements are designed for uniform distribution. The drag on the walls and floor results in zero velocity at these points, and the velocity exceeds the average at other points in the basin. The velocity is not stable because of varying density of the water, eddy currents, and volume of sludge. These factors are important in the determination of the dimensions of the basins.

SLUDGE STORAGE AND CLEANING

Unless sludge is removed continuously, allowance must be made in the basin volume for sludge accumulation between cleanings. In manually cleaned basins, coagulated matter may be allowed to accumulate until it tends to impair the settled-water quality, at which time the sludge is flushed out. Where the water is fairly turbid, the greatest depth of sediment is near the inlet end of the basin. There is no specified depth of sediment beyond which it should not be allowed to accumulate, but in the design of the basin an arbitrary depth is usually assumed as unavailable for settling.

As indicated previously, sedimentation basins which are not equipped for mechanical removal of sludge usually have sloping bottoms, so that when they are drained for cleaning, most of the sediment flows out with the water. Because the bulk of the material settles near the inlet end, the floor scope should be greater at this point. In some plants, sluice gates are arranged to deliver raw water to the sedimentation basin to flush out the sludge. The balance is generally washed out with a fire hose fitted with a small nozzle.

The time between cleanings varies from a few weeks, in plants that have short periods of settling and handle very turbid water, to a year or more, where the basin capacity is large and the water is not very turbid. Sometimes decomposition of organic matter in the sediment makes it desirable to clean a basin more often than would otherwise be necessary. Decomposition of certain types of sludge can be controlled by prechlorination or other chemical treatment.

SLUDGE REMOVAL DEVICES

Sedimentation basins may be equipped with sludge collection and removal mechanisms to maintain volumetric efficiency and reduce the need to shut down for cleaning.

Circular tanks may be provided with rotating mechanisms driven by motors mounted at the center of the tank or, in some plants, by motor carriages running on the wall of the tank and pulling the arms around. The rotating apparatus—equipped with rakes or blades that travel slowly around an axis, just above the floor of the basin—is designed to push the sediment to the center of the basin, where it is flushed out with a small stream of water. The bottom of the basin itself is given a fairly steep slope toward the center to facilitate the movement of the sludge. Square tanks may be equipped with a similar mechanism, except that two of the arms are often provided with outriggers which sweep into the corners of the tank outside of the radius of the circular area and convey the solids in those corners into the region of the main arms.

Two types of sludge-removal mechanisms are available for rectangular basins. One kind consists of a series of chains and sprockets, with the latter mounted at the top and bottom of the tank. Wood or steel cross members or flights are fitted between the chains. The flights scrape along the tank bottom, dragging the sludge to an outlet at one end. The second type of mechanism, mounted on a carriage which travels along the wall of the tank, does not have wearing parts under water and is thus less subject to shutdown. The sludge blades may be lifted and inspected at will without emptying the tanks.

Removal equipment must be designed to withstand the highly abrasive action of the sludge. In presedimentation basins where sand and grit is a problem and in softening plants where lime sludge is removed, careful design of blades is highly important, and wearing parts should be located above the water line.

SUSPENDED SOLIDS CONTACT CLARIFIERS

In recent years, increasing use has been made of basins which combine mixing, flocculation, conditioning, clarification, and sludge removal in a single unit. Coagulation takes place in the presence of previously formed

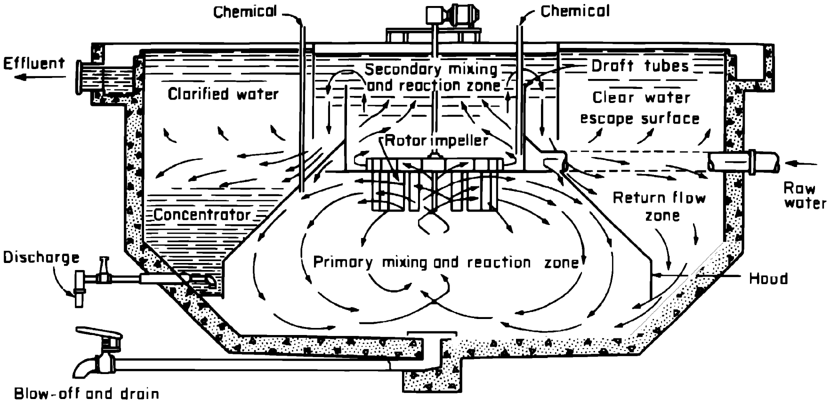

Fig. 18 An accelerator, combining chemical mixing, reaction, floc concentration, and clarification. *(By permission of Infilco.)*

floc which is retained in the unit to maintain a high floc volume concentration (see Fig. 18). As was discussed in the section dealing with mixing theory and flocculation, the presence of a high floc volume fraction greatly enhances the probability of particle collisions and, hence, the completeness of flocculation. Where softening is involved, the presence of preformed precipitates encourages further precipitation of hardness, thereby improving performance of the process. Excess solids are removed from the unit continually.

A major advantage for these units is the compactness of the multipurpose units. They require less space and may be less costly to install. However, the unitized nature of the construction generally results in a sacrifice in operating flexibility. A theory of operation for such clarifiers was advanced by Ives,[14] and an AWWA Committee Report[31] describes several types of equipment and discusses the advantages and disadvantages of such combination units.

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5

Chlorination and Other Disinfection Processes

By EDMUND J. LAUBUSCH

INTRODUCTION

Origin of Disinfection. The disinfection of water probably has been practiced for millennia, but obviously with little or no understanding at first of the principles involved in its improvement of water quality. Records show that the boiling of water clearly had been recommended by at least 500 B.C., but some historians[1] suggest that it probably had been employed from the beginning of civilization.

Until the germ theory of disease was established in the mid-1880s, odors were believed to be the means by which diseases were transmitted. It was also commonly held that the control of odors would limit the spread of infection. Thus, it was from this erroneous postulation that the disinfection of both water and sanitary wastes evolved.

Rationale of Disinfection. Water disinfection processes, as now ordinarily considered, involve *specialized* treatment for the destruction of harmful and otherwise objectionable organisms. Classically, disinfection processes have been employed for the purpose of destroying or inactivating disease-producing (pathogenic) organisms, more particularly bacteria, of intestinal origin. Such organisms that may appear in water may survive for weeks at temperatures near 70 °F or possibly for months at lower temperatures. In addition to the temperature factor, their survival in water depends on environmental, physiological, and morphological factors, including pH, oxygen, and nutrient supply dilution; competition with other organisms; resistance to toxic influences; ability to form spores; and others. Whether the organisms cause disease in man depends on how virulent they are, how concentrated they are, how they are ingested by the host, and how resistant the host is.

To illustrate the interrelationship of the several factors which influence the outcome when pathogenic organisms come in contact with a potentially susceptible host, Theobold Smith suggested the equation $D = NV/R$, where D is the probability of disease; N is the number of organisms; V is their virulence; and R is the resistance of the host. When the product NV is greater than R, disease results; when less than R, it probably will not. Some of the elements of this equation cannot, of course, be measured in numerical terms, but the equation does illustrate the situation. Moreover, it is applicable to the results of water disinfection since the values of N and V can be reduced (or even made equal to zero) by effective treatment.

Water disinfection obviously also encompasses destruction of disease-producing organisms other than intestinal bacteria, but it does not necessarily imply complete destruction of all living organisms, i.e., sterilization. Water disinfection processes are seldom carried to the point of sterilization, the latter being largely confined to medical practice.

Disease-producing organisms—other than bacteria—which merit attention in connection with water disinfection include a variety of viruses, intestinal protozoa, and some few macroorganisms. Additionally, many nuisance organisms of obvious aesthetic and economic significance, both plant and animal, are sometimes vulnerable to disinfection and can be partially or completely controlled by suitable treatment.[2] Important among the factors affecting the survival of these organisms in water, insofar as disinfection is concerned, is their natural resistance or imposed resistance (e.g., encasement in algae, suspended material, tubercules, etc.) to the disinfectants.

Efficiency of Disinfection. Among major factors influencing the efficiency of disinfection and, consequently, the kind of process employed in water treatment, are the following:

1. Kind and concentration of organisms to be destroyed
2. Kind and concentration of disinfectant
3. Contact time provided
4. Chemical character and temperature of the water to be treated

The resistivity of the same and of different kinds of organisms to a specific disinfecting chemical or agent varies considerably. Non-spore-forming bacteria are, for example, less resistant than spore formers (although the latter, generally, are of lesser sanitary significance). Cysts and viruses, on the other hand, are sometimes quite resistant, again varying among the same and different species and subspecies, and require treatment different in degree or kind from that required, for example, for most vegetative bacteria. Organism concentration is significant in that high numbers in a given volume (density) may create an unsatisfied demand; moreover, agglomeration or clumping of organisms, as previously implied, may present a barrier to adequate penetration of the disinfectant. In practice, no significant difference is generally observed between the hilling of high or low concentrations of organisms.

It is clearly apparent that no two disinfectants have the same germicidal capacity under a given set of conditions. In some cases the reaction of the material with water, as later discussed, might result in the formation of compounds of varying disinfecting efficiency; sometimes such compounds are completely ineffectual for disinfection. The kill of a species of organisms by a particular disinfectant, other factors being constant, is proportional to the concentration of disinfectant and the reaction time: the disinfectant is decreasingly ineffective as it becomes more dilute and as reaction time is decreased. With long contact times a low concentration of disinfectant might suffice, whereas with short contact times a higher concentration usually is required to accomplish equivalent kills.

Theoretically, in accordance with Chick's law,[3] the rate of kill of organisms is constant; in practice, however, the rate may actually increase or decrease with time. A decrease might be due to variations in resistivity of individual cells within the same species, a decrease in disinfectant concentration, or the presence of interferences and similar factors. An increase might be due to impeded penetration of the disinfectant into the cell and the dependence of kill rate upon the kind and concentration of disinfectant within the cell.

(The character of the water being treated has a marked influence on disinfection processes. For example, organisms surrounded by or embedded within suspended material may be impenetrable by chemical disinfectants and ultraviolet radiation. If the disinfectant is an oxidant, the presence of organic matter and other oxidizable material will deplete the amount of disinfectant available for attack on organisms, producing in some cases, compounds having diminished or no germicidal capacity. As will be discussed later, the halogens and many of their compounds hydrolyze and dissociate in water and may form one or a combination of other compounds that substantially differ in germicidal efficiency from the original material. In addition to the chemical character of the water, temperature influences the disinfection process; in general, the higher the temperature, the more rapid is the kill.

Means of Disinfection. Water disinfection can be accomplished by several means. Excluding those water-treatment processes that result in the partial removal of potentially infective or objectionable organisms (such as sedimentation, coagulation, filtration, etc.), the more specific water-disinfection processes of current significance include one or a combination of the following: (1) physical treatment, such as through storage or by the application of heat or other physical agents; (2) irradiation, such as by ultraviolet light; (3) metal ions, such as copper and silver; (4) alkalis and acids; (5) surface-active chemicals, such as quaternary ammonium compounds; and (6) oxidants, such as halogens, ozone, and other inorganic or organic materials.

Fair et al.[4] summarized criteria for appraising the suitability of various potential water disinfectants as follows:

1. Ability of the disinfectant to destroy the kinds and numbers of organisms present within the contact time available, the range of water temperatures encountered, and the anticipated fluctuations in composition, concentration, and condition of the water being treated
2. Ready and dependable availability of the disinfectant at reasonable cost and in a form conveniently, safely, and accurately applied
3. Ability of the disinfectant, in concentrations employed, to accomplish the desired objectives without rendering the water toxic or objectionable, aesthetically or otherwise, for the purpose it is intended
4. Ability of the disinfectant to persist in residual concentrations as a safeguard against recontamination where this might be important (such as potable-water distribution systems)
5. Adaptability of practical, duplicable, quick, and accurate assay techniques for determining disinfection concentration, for operating control of the treatment process, and as a measure of disinfecting efficiency

Except for chlorine and some of its compounds (and heat in the case of individual water systems), most other of the few water disinfectants herein mentioned currently have one or more serious limitations that preclude their general acceptance and adaptability for municipal potable-water treatment operations.

WATER DISINFECTANTS OTHER THAN CHLORINE

Heat and Other Physical Agents. The important waterborne diseases are not known to be caused by spore-forming bacteria or other heat-resistant organisms, and therefore water can be disinfected by subjecting it to heat. Emergency "boil water" orders issued by many utilities in times of emergency are predicated upon the fact that water can be rendered potable by subjecting it to boiling temperature for about 15 to 20 min. The method is, however, impractical on a routine or large-scale basis.

Analogous to the long-established procedures for pasteurization of milk and milk products, Goldstein et al.[5] recently described a continuous-flow water pasteurizer applicable for treating farm ponds, cisterns, and other similar individual domestic water-supply sources. The heart of the 250-gal-per-12-hr unit is a heat exchanger that recovers all but 10 °F of the heat required for treatment and that allows pasteurization of water at 161 °C for 15 sec. Demonstrated effective even with a very high bacterial concentration in the raw water, total cost of household-scale treatment was estimated at about $1 per 1,000 gal. The principal advantages indicated are reliability and simplicity; disadvantages are the lack of residual disinfection action and high cost.

The physical and biological effects of ultrasonic frequency waves have been the subject of laboratory investigations at least since 1926.[6] (Ultrasonic frequencies, to which the ear does not respond, occur above 18,000 cps.) Horwood et al.[7] in the United States demonstrated in 1951 the lethal effects of ultrasonic energy at 400 kc/sec on aqueous suspensions of *E. coli*; at 98 °F complete sterility was obtained after sonoration for 60 min. Horton et al.,[8] in further pursuit of the research, estimated that operating costs would approximate $15,000 to sterilize one million gal of 140 °F water and concluded that ultrasonics have little or no practical application to domestic water treatment. At University College in London, England, a 3-year research program to determine the applicability of ultrasonics to water treatment was terminated in 1952, also on grounds that efficiency was considered too low to compete with existing disinfecting processes. In the U.S.S.R., the Academy of Communal Economy undertook, from 1954 to 1956, an extensive study of the bactericidal properties of ultrasonic waves on raw river water and *E. coli*-inoculated tap water. The results indicated that regardless of the high bactericidal effect, the method was impractical and uneconomical because of the high consumption of electric energy.[9] Falkovskaja[10] later described investigations of the effects on *B. coli, B. aerogenes*, and *B. subtilis* which indicated that bactericidal action was not affected by turbidity or by the thickness of the water layer up to 10 cm; that action, dependent mainly on intensity, was equally great on vegetative and spore-forming organisms; and that the main mass of bacteria was killed by exposure for 2 to 5 sec. In 1960, Elpiner[11] presented data of an experimental study aimed at shortening exposure time and increasing the volume of water disinfected per unit of time. He determined that this could be effected by increasing intensity of the sound and by augmenting treatment with ultraviolet rays.

Irradiation. The ultraviolet method of disinfection involves exposure of a film of water (up to about 120 mm thick) to one or several quartz mercury-vapor arc lamps emitting germicidal ultraviolet radiation at a wavelength in the range between 200 and 295 mμ Contemporary UV units, unlike earlier models, can operate on standard 100 volts ac, and usually emit 25 to 30 per cent of their energy in the spectral region of 2537 Å.

Baker[1] has indicated that the earliest known positive mention of the successful application of ultraviolet-ray water disinfection was in 1877 and that in 1909 to 1910, ultraviolet-ray apparatus was experimentally operated at Marseilles, France, in competition with several types of filtration and purification works. In the United States, the first known municipal installation of ultraviolet-ray apparatus was at Henderson, Kentucky, in 1916. Between then and 1928, three other municipal installations were made, but all had been abandoned by 1939, primarily because of the greater cost of operation and maintenance compared with other disinfection processes and the inadequacy of apparatus then available.[12] Carlson et al.[13] reported in 1942 that UV irradiation was more effective in destroying polio virus in water than coagulation and sedimentation, filtration, activated charcoal, or storage; but their results cannot be considered a quantitative measure of the effectiveness of these methods.

In more recent times Kelly[14] demonstrated applicability of two UV units to small-scale commercial seawater purification installations; in seawater (having a turbidity up to 20 ppm) seeded with sewage and having an average coliform MPN as high as 580 per 100 ml, 99.96 per cent coliform reduction was accomplished. Gilcreas et al.[15,16] reported on the experimental use of a commercial UV unit comprising six 30-watt 2537-Å ultraviolet lamps that permitted treatment of up to 750 gal/hr at an exposure of about 4.2 sec and a flow depth of about ⅜ in. Various conditions of operation and water quality were investigated, and complete coliform destruction was observed with (inorganic) turbidity up to 125 ppm and (inorganic) color up to 75 ppm at optimum operation of the UV unit. These investigators also reported greater resistance of certain viruses, other than *E. coli*, to ultraviolet radiation.

In Germany and Great Britain ultraviolet disinfection is now known to have been applied to public water supplies.[7] Zimmerman[17] reported on the successful 1-year use of two UV mercury low-pressure lamps to irradiate a small water supply. The raw water, which was high in both hardness and bacterial count and contained 0.3 mg/l iron, flowed in a 3- to 4-cm layer over the lamps at a rate of 18 cu m/hr. In Great Britain the results of investigation by Standen and Fuller[18] of the effect of UV radiation from mercury resonance lamps (in the region of 2537 Å) on the cercaria of *Schistosoma mansoni* (blood fluke) indicated that 4- to 8-sec exposure completely inhibited development of the organism to the adult stage. In France, where investigations of UV for disinfection were pioneered, applications are reportedly limited to small installations.[9] It has been reported that UV treatment is widely practiced in the Soviet Union. [9] Applications appear limited, however, to individual or small communal systems, and practical application to large waterworks remains unsolved. Systems proposed by the Academy of Communal Economy for large waterworks entail the arrangement of several lamps in series inside a conduit through which filtered water flows into a storage reservoir.

Existing United States applications of ultraviolet disinfection apparently are largely limited to smaller institutional and industrial supplies and to a few swimming pool waters, especially when used in conjunction with other disinfectants.

Some of the advantages and disadvantages of UV for disinfection of potable water are:

Advantages	*Disadvantages*
1. Foreign matter is not introduced into water and physical or chemical character is not significantly affected.	1. Spores, cysts, and viruses are less susceptible than are vegetative bacteria.
2. Constituents of the water in solution, such as ammonia, exert no effect on disinfecting capacity.	2. Thorough water preconditioning is required because UV is absorbed by many constituents normal even to pretreated waters.
3. Tastes or odors are not produced (but UV has no effect on removal of odor or color).	3. Residual disinfecting capacity apparently is not provided.
4. Short contact periods (exposure time) are effective.	4. Extensive amounts of electric energy and expensive equipment are required.
5. Overdosing produces no detrimental effects.	5. Frequent and expensive apparatus maintenance is necessary to ensure stable energy application and essentially uniform density throughout effective radiation area. Treatment efficiency is not readily determinable (lack of rapid field test).

The increasing availability of radioactive materials has stimulated some interest in disinfection by ionizing radiations. Little information is available, however, on the destruction of water organisms by this means. Even with a relatively cheap source of radiation, the use of disinfecting dosages of beta and gamma radiation would seem to be restricted. However, the accelerated development of the nuclear-power industry and wastes therefrom suggests the possibility of the future potential of this disinfectant source for water (and wastewater, particularly) treatment.[19–21]

Metal Ions. It has been known for many centuries that copper is bactericidal (only weakly so) and strongly algicidal. Other metals, such as mercury and silver, are also notably effective in minute concentrations. The name "oligodynamic" or "forces of trifles" has been given to the sterilizing action of minute quantities of such metals.[22]

The oligodynamic properties of silver were described by Raulin in 1869,[23] and in 1893 Nageli, a Swiss botanist,[22] observed the disappearance of *Spirogyrae* from waters containing minute quantities of finely divided silver precipitated from one of its salts. The common use of silver for surgical instruments and for the impregnation of bandages and ointments, and the use of silver nitrate, argyrol, and other forms of colloidal silver suspensions for treatment of various body infections are well established.

Silver is a soft, lustrous, white metal that is insoluble in water and alkalis. Its particular affinity for sulfur and halogen elements is well recognized, the reaction with sulfur (resulting in the formation of silver sulfide) and with iodine (to form silver iodide) being widely used in numerous analytical assay techniques. Silver is readily ionized by electrolysis, and this property is the basis for some systems used in the disinfection of water. The rate at which silver is ionized is directly related to the amount of current applied. Dosage can be increased or decreased by varying the current flow (concentrations considered for water treatment are in the range of 25 to 75 ppb).

In addition to application by electrolytic decomposition of the metallic element, silver can be applied as a solution of its salt or by desorption from filter beds of silver-coated sand, carbon, fabric, or other coated silver-releasing materials. Crystalline silver nitrate, $AgNO_3$, a form sometimes employed in connection with water treatment, is extremely caustic to moist skin and mucous membranes. Aqueous solutions of the compound are also strongly irritating, and care must be exercised in their handling. "Public Health Service Drinking Water Standards"[24] limit the concentration of silver in potable waters to 0.05 mg/l (50 ppb).

Baker[1] indicated that the first paper in English on the use of silver for water disinfection was published in 1932 in England, and that four papers on the subject were published in the United States between 1934 and 1936, one originating in Russia and another in Poland. The former deal with laboratory experiments with silver-coated sand, and the latter deal with experiments with "filters containing metallic silver, with solutions of silver salt and with electrocatynization," whereby finely divided silver was produced by an electrolytic system. In 1937, Shapiro and Hale[25] reported that the time required for effective disinfection was long, both in the laboratory and at swimming pools in New York City, and that chlorides, ammonia, and other organic matter interfered with the treatment efficacy.

In 1949, Newton and Jones[26] reviewed several reports on the bactericidal capacity of silver and noted that while the effective minimum concentration and exposure periods reported varied considerably, concentration generally was of a low order of magnitude. These investigators evaluated the cysticidal properties of silver ions on *Endamoeba histolytica* and concluded that concentrations and exposure periods required appear to be considerably in excess of those usually suggested for the treatment of drinking water supplies. During the 1950s there was considerable and renewed interest in the use of silver as a water disinfectant, particularly for small water supplies. Renn[27] extensively studied a Swiss product, Hyla 603K, containing silver-donating filtration material and reported it highly bactericidal in low concentrations (although not cysticidal). Chang and Baxter,[28] however, demonstrated that Ag^+ ion at a concentration of 97 ppm (150 ppm $AgNO_3$) has a cysticidal efficiency equivalent to approximately two-thirds that of 10 ppm of I_2. In evaluating environmental factors influencing the efficacy of a United States product, Movidyn, Chambers et al.[29] observed that the relationship of the disinfectant to bactericidal action appears to deviate from the accepted pattern of phenolic and halogen disinfectants to a degree greater than that explainable by experimental errors of the technique used and is less in certain test waters than in others. Chambers et al.[30] later demonstrated that the germicidal action of silver is related to the concentration of silver ions rather than to the physical nature of silver from which the ions are derived (contrary to some earlier reports that silver added as a colloidal suspension by filter beds or electrolytic devices is more germicidal than an equivalent amount of silver applied as silver nitrate). These investigators also demonstrated that in the presence of inefficient neutralizers (such as sodium thiosulfate), bacteriostasis may be mistaken for bactericidal action. In a report issued by the U.S. Public Health Service in 1962,[31] it was observed that because of its relative expense, adsorption and bacteriostasis characteristics, long reaction time, and other factors silver is not a very useful disinfectant in large applications; the report noted, however, that it might be useful in specific, small applications (e.g., swimming pools).

The application of silver as a water disinfectant elsewhere also does not appear to be extensive. In Austria and Belgium, silver reportedly is used in isolated instances at private water-supply installations; in France, its use is said to be mainly limited to the food and carbonated beverages industry; in the U.S.S.R., the Laboratory of Water Chemistry and Technology of the Academy of Science of the Ukrainian S.S.R. is said to have developed stationary and portable apparatus for the production of silver and its concentrates for the disinfection of village water supplies.[9]

Some of the advantages and disadvantages of silver for potable-water disinfection are:

Advantages

1. Low disinfectant concentrations are effective against vegetative bacteria if skillfully and properly employed.
2. Powerful, long-lasting residual bacteriostatic action is provided.

Disadvantages

1. Thorough water pretreatment is required, as turbidity, organic color, and other colloidal suspended matter adsorb Ag^+.
2. Certain biological species (e.g.,

3. Light and variations in organism concentration appear not to affect germicidal capacity.
4. Growth of certain algae and fungi is inhibited.
5. Proprietary disinfectants are tasteless, nonpoisonous, and relatively easily handled.

anaerobes, cysts, spores, algae) are resistant; some organisms may habituate themselves to action.

3. Germicidal action is markedly decreased at cold temperatures and low pH levels.
4. Phosphates, chlorides, sulfides, and sulfates inhibit action.
5. Adsorption on contact surfaces reduces available disinfection concentration.
6. Practical, reliable tests for determining low Ag^+ concentrations have not been sufficiently well developed.
7. Relatively long contact periods are required.
8. Treatment is costly (about 200 times higher than gaseous chlorine).

Alkalis and Acids. Pathogenic bacteria normally do not survive long in strongly alkaline or acid waters. Though of only very limited direct interest as disinfectants, the application of certain materials for pH and corrosion control, lime softening, etc., can effect a partial reduction of some microorganisms in water, especially where long contact periods are available.

Surface-active Chemicals. Cationic detergents are highly germicidal, but anionic detergents are only weakly so; neutral detergents occupy an intermediate position. Quaternary ammonium compounds (QAC), known since 1916, include a wide range of cationic detergents that readily ionize in water. Obtainable as liquids or solids that are stable at ordinary temperatures, they lower the surface tension of water and tend to foam profusely unless highly diluted.

Each QAC is a distinct chemical entity having distinct germicidal capacity. Their mode of action as disinfectants is considered different from that of gaseous chlorine. Chambers et al.[32,33] reviewed the general germicidal capacity of QAC and the effects of various environmental factors influencing germicidal efficiency. They noted that most proprietary QAC have superior germicidal capacity in pH ranges of 7.0 to 8.5 to 9.0, and that germicidal efficiency is markedly affected by such factors as the nature of additives used in the QAC formulation and by certain mineral and water hardness characteristics. Research is hampered by lack of a quantitative chemical test of residual QAC formulation and by certain mineral and water hardness characteristics. Research is hampered by lack of a quantitative chemical test of residual QAC that can be interpreted in terms of germicidal effect. Chambers[34] recently approximated the treatment cost of one proprietary QAC at about 70 times that of chlorine at dosage concentrations of 1 ppm each.

QAC have not been seriously considered for use as potable-water disinfectants partially because of limitations already implied, their possible toxic effects, and objectionable tastes they impart. The current U.S. Public Health Service attitude is that it is unlikely that they would be acceptable in drinking water.[35] (Current Food and Drug Administration regulations preclude their use in milk and food products.) They have been suggested, and are selectively employed in a limited degree, for specialized applications such as swimming pool algicides, for water-main disinfection, and to control growth of fouling organisms in industrial cooling water systems.[35,36]

Chemical Oxidants. Of these materials, the halogens such as bromine, iodine, and chlorine, released in suitable form from various sources, are the most widely used. Because chlorine and some of its compounds are so effective and almost universally employed as disinfectants, they will be treated separately, and in detail, later in this chapter. Indeed, in contemporary water-treatment technology the terms "disinfection" and "chlorination" are popularly applied interchangeably, at least in North America and especially in the United States.

Bromine. Bromine, Br_2, is a dark, reddish-brown halogen that exists as a liquid at atmospheric pressure and is, therefore, less cumbersome to handle than compressed gas. About 3.2 times heavier than water, it has a melting point of 7.3 °C and a boiling point of 58.7 °C. It is commercially available in 1-lb and 6½-lb glass and earthenware bottles. It produces fumes that are very irritating, and the liquid causes severe burns on contact with the skin.

Slightly soluble in water, bromine is a good germicidal agent, and effective tests are available for determining residual concentrations. As is the case with chlorine, amino forms are produced in the presence of ammonia and other trivalent nitrogenous materials, and a similar breakpoint phenomenon has been demonstrated. Bromine and monobromamine have been reported nearly equal in bactericidal properties and essentially equal to free chlorine on a part-per-million basis at comparable pH.[37]

There are no known applications of bromine to public water supplies. Applications appear to be limited to the treatment of swimming pools and industrial waters. The efforts and experiences of the Illinois Department of Health relating to bromination of swimming pools (begun about 1940) are well known. Some of the advantages that have been reported are: (1) certain forms are easier and less hazardous than chlorine to handle and store; (2) the bactericidal efficiency of bromamines, formed under pool conditions, is superior to chloramines; (3) there is an apparent reduction of eye irritation; and (4) odors are not troublesome. Additional investigation of its bactericidal activity, the effects of various environmental influences, control procedures, material and equipment problems, and the economics of its use are prerequisites to any recommendation for its use in potable-water treatment.

Iodine. Commercial iodine is a volatile, purplish-black, crystalline solid which is corrosive to most common metals and which sublimates slowly at normal atmospheric conditions. When heated, it forms a violet, toxic vapor that is less hazardous than other halogens used in water treatment. At room temperature the solubility of iodine in ethyl alcohol is 27.0 per cent; in water, it is about 0.03 per cent (the latter can be substantially increased by adding iodide, but the problem is especially critical at low temperatures).

Common commercial iodine preparations contain added iodide to improve their stability and solubility. When such preparations are dissolved in water, the I_2 may remain in its elemental form, or it may undergo various complex changes, depending on the initial concentration of titrable iodine and added iodide and the pH and temperature of the solution. Hydrolysis occurs in accord with

$$I_2 + H_2O \qquad HOI + H^+ + I^- \tag{1}$$

Chang[28] has demonstrated that in a 25 °C solution of elemental iodine containing 0.5 ppm total titrable iodine and sufficient iodide so that the I_2:I^- molar ratio is 1:1.2, an insignificant amount of I_2 is hydrolyzed until the pH rises to 7.0 or above. These relationships are illustrated in Fig. 1. When the pH is increased to 8.0, the amount of I_2 hydrolyzed to hypoiodous acid ranges from 20 to 90 per cent at titrable iodine concentrations of 20 to 30 ppm and 0.5 ppm, respectively. Both I_2 and HOI are germicidal. Hypoiodous acid decomposes to a nongermicidal iodate, and iodide forms at pH levels of 9.0 and over, especially in the presence of phosphates. In the presence of added iodide in an aqueous solution, some bactericidally inactive tri-iodide (I_3^-) can be formed, but the amount is essentially insignificant when the initial total titrable iodine concentration is 20 ppm or less and pH levels are below 7.0. See also Ref. 38.

Impetus to the use of iodide for water treatment is said to have developed in the early 1920s when it was suggested that small amounts added to water at infrequent intervals would prevent goiter.[1] In 1923, Rochester, New York and Sault Sainte Marie, Michigan, began adding iodide to the public water supply for this purpose; at Rochester the practice was continued for 10 years, while at Sault Sainte Marie it was applied only briefly. Iodization was also practiced from 1924 to 1925 at Derbyshire, England. Public apathy, opposition by secular and professional groups, and the practice of iodizing normal table salt, also begun in 1923, precluded further development of iodizing water.

According to Gershenfeld and Fox[39] the possibility of using an iodine

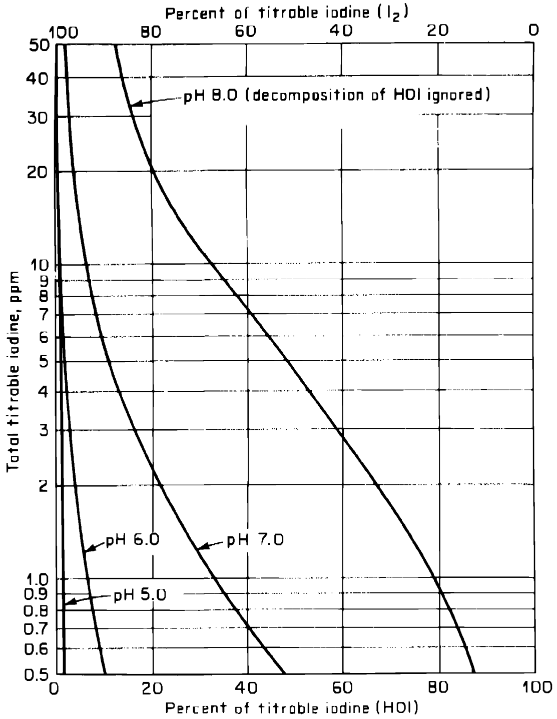

Fig. 1 Distribution of I_2 and HOI in 25 °C water at indicated pH levels.[51]

tincture for the rapid sterilization of drinking water was suggested by Vergnoux in 1915. Gershenfeld also refers to reports by Bachman and Hinman on experimental applications of iodine from 1917 to 1918 to destroy disease-producing bacteria in water. In 1922, Hitchens[40] of the U.S. Public Health Service recommended the use of tincture of iodine for emergency disinfection of drinking water supplies (see also Ref. 41). In 1933, Beckwith and Moser[42] compared the efficiencies of chlorine, bromine, and iodine in destroying *E. coli*, but their investigations were hampered by lack of a satisfactory method for quantitative determination of low iodine residuals. Pond and Willard[43] reported in 1937 that two drops per liter of a 7% iodine tincture made drinking water safe within 15 min.

In 1941, the Office of Scientific Research and Development of the National Research Council contracted with Harvard University for the development of a method of disinfecting canteen water supplies which would destroy amoebic cysts as well as enteric pathogenic bacteria. In the course of investigations in which a large number of active halogen compounds, including chlorine-containing Halazone tablets, were evaluated, it became evident that iodine-containing compounds might more nearly satisfy military requirements as a field disinfectant, and intensive research of iodine disinfection was undertaken. By 1945, a stable tablet preparation (Globaline, containing tetraglycine hydroperiodide and releasing 8 to 9 ppm I_2 in a quart of water) had been developed and demonstrated effective for destruction of enteric bacteria, amoebic cysts, and cercariae of schistosoma using one or two tablets per quart and a 10-min contact period, depending on the color and temperature of the water. Some concern was expressed regarding possible adverse physiological effects of prolonged ingestion of iodine. To evaluate this the Army and Navy conducted extended field tests from 1949 to 1950 in the Marshall Islands (where temperature and humidity are high), using sodium iodide as the iodine source; no evidence contraindicating iodine ingestion of 12 to 20 mg/day over a 6-month period was observed.[44] In 1950, the National Research Council recommended military development and use of a standardized iodine compound for disinfection of individual drinking water canteens,[45] and the Globaline preparation developed and recommended earlier by Morris et al.[46] at Harvard was thereupon adopted by the military to replace Halazone tablets used previously.

Stimulated by the interest of the military and the progress of the Harvard investigations, Chambers et al.[47] of the U.S. Public Health Service also investigated the effects of various environmental factors on the bactericidal action of low dosages of iodine (at residual concentrations of 0.2 ppm and greater). They reported that, as with chlorine, a combination of low temperature and high pH is least conducive to efficient disinfection; that higher concentrations of iodine than chlorine generally are required to produce comparable bactericidal kills under similar conditions; and that the effect of changing pH is generally of low magnitude except at low temperatures. This observation also was made by Chang and others[28,48–53] who extended their investigations to the efficacy of iodine against cysts, schistosoma cercariae, leptospira, and viruses.

Since the mid-1950s, numerous reports[48–53] have been published on the chemical and germicidal properties of various forms of iodine, especially hypoiodous acid and diatomic iodine. Chang's investigations[28,51] indicate that I_2 is more cysticidal than either HOI or I_3^-, the cysticidal efficiency at 6 and 25 °C of HOI being about one-third and one-half of that of I_2, respectively, and of I_3^- being about one-eleventh and one-eighth of that of I_2, respectively; that nonbactericidal IO_3^- also exhibits little or no cysticidal effect; that HOI is more viricidal than I_2; and that both I_3^- and IO_3^- are apparently nonviricidal. The differences in relative cysticidal and viricidal efficiencies of iodine at 25 °C and at various contact periods are suggested by data in Table 5-1.

TABLE 5-1 Relative Cysticidal and Viricidal Efficiencies of Iodine at 25°C[51]

Contact time, min	I_2 residuals, ppm	
	Cysticidal	Viricidal
10	3.7	6.3
5	6.0	13.6
2	12.5	34.0

The possible toxic and physiological effects of iodine appear not to have been sufficiently explored to justify uses other than its emergency use as a potable-water disinfectant. Since 1958, however, various investigators[54–56] have reported on research and field applications of iodine as a swimming pool disinfectant. Most of these investigators observed iodine to be effective for disinfection of swimming pool waters over a wide range of pH and other conditions. For this purpose, iodine can be applied in the form of a sodium and potassium salt, as one of the organic complexes, or as elemental iodine. When iodine salts are used, elemental iodine usually is released through the application of chlorine or hypochlorites.

Some of the advantages and disadvantages of iodine as a disinfectant are:

Advantages

1. Bactericidal capacity is not greatly influenced by pH except at very low temperatures.
2. Ammonia and organic nitrogenous impurities have little effect on germicidal efficiency because they do not form substitution compounds with iodine.
3. Action depends less on contact time and temperature than for chlorine.
4. Effective against more pathogenic organisms (including spores, cysts, viruses, etc.) within short times and at relatively low dosages.
5. Persistence of residuals appears to be less dependent upon bather load than are chlorine residuals.
6. Complaints of tastes, odors and eye, ear, and skin irritations are infrequent when properly used for disinfection of pools.

Disadvantages

1. Higher concentrations than for chlorine on a ppm basis are necessary to produce comparable bacterial kills under similar conditions.
2. Organic color and other reducing materials substantially affect germicidal action (but the effect is generally less marked than on free chlorine).
3. Expensive—about 20 times higher than chlorine per unit of germicidal effectiveness.
4. Taste and slight color produced can affect palatability and aesthetic quality.
5. The relative germicidal efficiencies of various iodine forms are not fully established.
6. Preparation of stock iodine solutions (alcohol or water) currently is impractical and economically prohibitive on a large scale.
7. Physiological effect of prolonged use, especially in children, remains to be ascertained.

Ozone. Ozone, a faintly blue, pungent-smelling, unstable gas, is an allotropic form of oxygen in which three atoms of the element are combined to form a molecule, O_3. Because of its instability and characteristics, it is generated almost invariably at the point of use. The resulting ozone-air mixture thus generated can be admitted to water by spraying the water into an ozone-containing atmosphere, by discharging the ozonized air into a scrubber, or by applying the ozone-air mixture through an injector or diffusing it upward into the water in a well-baffled mixing chamber.

Discovered in 1783 by the Dutch scientist Van Marum, it was dubbed "ozone" in 1840 by Schönbein (from a Greek word meaning smell), who is said to have experimented with it for treating water at Metz, Germany. According to Hann,[57,58] the earliest investigations of ozone for municipal water treatment were undertaken late in the nineteenth century in Germany, Holland, and France. Ohmüller reported that ozone effectively destroyed typhoid and cholera bacteria at the semicommercial plant installed by Frölich at Martinikenfeld in 1891,[59] and this led to full-scale municipal installations at Wiesbaden and Paderborn in 1896. In this same period Van Ermengen and Calmette and Roux[60,61] reported extensively on results of treatment at Oudshoorn, Holland, indicating the effectiveness of ozone against all spores and pathogenic and saprophytic bacteria encountered. These investigations led to the adoption of ozone treatment at plants in Paris, Lille, and Nice, France (1898 to 1904). By 1933, the Paris installations were treating about 90 mgd of water by ozone. In a dissertation on industrial applications of ozone published by Hartman[62] in 1924, it was reported that water supplies of Madrid, Vienna, and numerous provincial cities and towns of France and Germany were being purified by ozone. In Russia, ozone facilities are said to have been installed in 1905 to 1906 at Tzarskoe Selo. At Petrograd (St. Petersburg), ozone disinfection of a 13-mgd supply was in operation between 1911 and 1919.[9] In England, experiments by the London Metropolitan Water Board on a portion of the city's supply led, in 1933 and upon the advice of Sir Alexander Houston, to the installation of ozonators at one facility treating 10 to 15 mgd.[63]

In a detailed review of the development of American interests in ozonation, Baker[1] noted the research by Soper in the late 1890s, who concluded that "drinking water can be sterilized, and that unpleasant colors and odors arising from organic impurities can be removed by ozone." Baker mentioned briefly the few United States municipal applications of ozone (primarily for taste, odor, and color control) at the New York City Jerome Park Reservoir (1906), Ann Arbor, Michigan (1909 to 1910 to 1914), Baltimore, Maryland, County Electric Water Co. (1910 to 1918), Ogdensburg, New York (0.075 mgd, from 1927 to 1930), Delhi, New York (1928 to 1935), Long Beach, Indiana (1930 to about 1950), Hobart, Indiana (1932 to about 1953), Whiting, Indiana (1940 to present), Denver, Pennsylvania

(0.03 mgd, from 1940 to 1942 and later), the Lower Roxborough (1 mgd) station of Philadelphia, Pennsylvania, waterworks (1941 and 1942). The ozone equipment installed at Whiting[64] was designed specifically for taste and odor control. Ozonation, in combination with other treatment processes, is still in use there (1963) and is reportedly producing an acceptable water from a very difficult-to-treat water source; postchlorination is, however, required by the Indiana State Board of Health.[65]

Based on the results of ozone treatment of a 2-gpm pilot plant operated from 1941 to 1942 at Philadelphia's Lower Roxborough, Torresdale, and Belmont facilities with approval of the Pennsylvania State Board of Health, fifty 25 lb/day ozone generators were installed in 1949 at the 36-mgd Belmont rapid-sand filter plant (at a cost approximating $600,000).[66] As in Indiana, the state health authorities also required postfiltration and postchlorination treatment. This plant, treating Schuylkill River water then containing large amounts of coal, acid, organic derivatives, color, and turbidity, effected a 45 to 70 per cent reduction in odors, as measured by the standard threshold method, during its first 4 years of operation; musty odors and tastes of natural organic origin, however, were not so effectively reduced. Manganese reductions averaging 70 to 80 per cent were obtained with ozone residuals of 0.15 to 0.20 ppm, as compared with about 40 per cent reduction without ozone treatment. Coliform reductions reportedly averaged 95 per cent with an ozone residual of less than 0.1 ppm and 99 per cent with residuals of 0.2 ppm and above. In May, 1959, with the Belmont plant rehabilitated and capacity increased to 108 mgd, ozone operation was terminated and replaced by excess chlorination, which had been demonstrated effective on the Schuylkill River water, the quality of which had been steadily improved during the 1950s.[67]

More recently, Killam[68] reported the use of a pilot-scale microstraining unit in combination with ozonation for reduction of color, taste, and odor at Danvers, Massachussetts, where four 25-lb ozonators (reportedly approximating $72,500) were found "entirely practicable and effective in reducing color to any desired amount." In Canada, Norbert[69] reported in connection with five municipal waterworks in Quebec Province that ozone effects water of good quality, free from tastes and odors that had not been removed by prior treatment with chlorine and activated carbon.

Despite the numerous plant applications, especially in Europe, and favorable reports on the value of ozone for disinfection, until relatively recently there has been a paucity of data on quantitative aspects of the subject. In reports of the comparative bactericidal efficiency of ozone and chlorine, Smith and Bodkin,[70] Buffle,[71] and others[72] noted the faster action of ozone and the lesser influence of pH and temperature than for chlorine. These observations were confirmed by Leiguarda et al.[73] who reported also that, part for part, chlorine is more active on vegetative forms of *Cl. perfringes*, but that ozone is more active against the spores. As to comparative cysticidal efficiency, Kessel et al.[74] reported that 0.3 ppm ozone acted several times faster against *E. histolytica* than chlorine; Hettche and Schulz-Ehlbeck[75] also reported superior cysticidal capacity of ozone as compared to free chlorine. Kessel et al.[76] reported that the same quantity of a polio virus was destroyed in 2 min by 0.05 to 0.45 mg/l ozone as in 1½ to 3 hr by 0.5 to 1.0 mg/l chlorine residual (probably combined). Lagrange and Rayet[77] reported a 100 per cent kill of *S. mansoni* cercariae in 3 min when subjected to 0.9 ppm ozone and in 4 min when subjected to 1 ppm chlorine.

Methods for determining ozone in water have been reported by Ingols et al.[34,78] and by Stumm.[79]

There are more ozonation water-treating facilities in France than in any other country. Of the approximately 1,000 public water supply facilities in Great Britain relatively few use ozone. Elsewhere in Europe only a few ozone installations are reported to exist. The rapid and extensive development of electric energy in the Soviet Union has resulted in renewed interest there, and plans are reported in progress for the installation of a number of ozonators at waterworks in that country.[9] There is no evidence of renewed interest in the United States in ozone as a water disinfectant, although some evaluations of its use for wastes treatment are in progress. The development of breakpoint chlorination and its wide success for handling most taste and odor problems, the introduction and development of chlorine dioxide treatment, the inability of ozone to exist as a residual in distribution systems, and the generally high electric energy requirements and costs are among the factors contributing to the greater popularity of materials other than ozone for disinfection and taste, odor, and color control.

Some of the advantages and disadvantages of ozone as a disinfectant are:

Advantages

1. Complex taste, odor, and color problems are effectively reduced or eliminated.
2. It is a powerful oxidant that rapidly oxidizes organic impurities.
3. Disinfecting action is effective over a wide temperature and pH range.
4. Bactericidal and sporicidal action is rapid (said to be from 300 to 3,000 times quicker than chlorine), and only short contact periods are required.
5. Odors are not created or intensified through formation of addition or substitution complexes.

Disadvantages

1. No lasting residual disinfecting action is provided.
2. Electric energy requirements and capital and operating costs are high (about 10 to 15 times higher than chlorine).
3. The ozone-air mixture produced by necessary on-site generation is only slightly soluble in water, and production is complicated when temperature and humidity are high.
4. Process is less flexible than chlorine in adjusting for flow rate and water quality variations.
5. Analytic techniques are not suffi-

6. There is no possibility of danger or harm from overtreating.

ciently specific or sensitive for ready and efficient control of the process.

6. Waters of high organic and algal content usually require thorough pretreatment to satisfy the ozone demand.

Miscellaneous. Potassium permanganate, $KMnO_4$, is a powerful oxidant, but its application in water treatment specifically for the purpose of disinfection is rare. According to Banerjea[80] a concentration of 2 mg/l and a 24-hr contact period is necessary to ensure satisfactory results. Reports of another strong oxidant, hydrogen peroxide, H_2O_2, suggest its inferior capacity as a water disinfectant.[81–83]

DEVELOPMENT OF WATER CHLORINATION

Chlorine as a Deodorant. Chlorine was discovered in 1774 by a Swedish chemist, Karl Wilhelm Scheele, as a product of the reaction of hydrochloric acid and manganese dioxide. The gas was first liquefied in 1805 to 1806 by Thomas Northmore and was first identified as an element by Sir Humphrey Davy, who named it from the Greek word *cloros* (meaning green) because of its characteristic color. History records its use as a general disinfectant at about 1800 by De Morveau in France and by Cruikshank in England.[84]

Just when chlorine was first used specifically to improve water quality is not clear, but there is no question that the earliest applications were advocated on the basis of its deodorizing capacity and not its disinfecting capacity. The literature records that sometime prior to 1835 it had been proposed to add a small quantity of chlorine or one of the chlorides to make water of marshes palatable. In commenting on this proposal a Scottish-American physician observed, " . . . a quantity [of chlorine] sufficient to destroy the foulness of the fluid can hardly fail to communicate a taste and smell disagreeable to most individuals."[1] Such were the early murmurs, that unfortunately persist in some areas, concerning chlorinous tastes and odors. Bleach solutions (probably sodium hypochlorite) were, however, being used by 1850 to treat well waters,[84] but, again, apparently without definite knowledge of its capacity to destroy microorganisms.

Just when chlorine or its compounds were first used in connection with wastes treatment is also unclear. As early as 1830, the use of chloride of lime for deodorizing sanitary waste systems had been advocated, and was practiced to some extent.[85,86] In 1854, chlorinated lime was being used in England by the Royal Sewage Commission to deodorize London sewage, and its use in that country to treat body wastes from typhoid patients before disposal to sewers was described in 1879.[85,87]

During the last half of the nineteenth century dozens of American and British patents were granted covering various materials and processes applicable to water and wastes treatment. Most of these patents related to the use of voltaic action, magnetic action, or electric currents, and some few related to the use of chemical oxidants such as chlorine, permanganates, and hypochlorites. In 1887, a British patent was obtained by Webster for "methods of purifying sewage and other impure water." (No record of use in the latter connection is apparently recorded.) Few patents, however, resulted in plant-scale applications of the processes involved.[1] "Electrozone," chlorine produced from electrolysis of salt brine, was applied to sewage at Brewster, New York, in 1893, prior to discharge into the Croton River.[88,89]

Chlorine as a Disinfectant. None of the proponents of electrolytic processes claimed that electrocution of bacteria was involved, but even some eminent scientists of that era did not recognize that the electrolytic production of chlorine or another oxidizing material was the underlying principle. Commenting on one of the processes, Professor T. M. Drown, who recognized it simply as disinfection by electrolytically produced sodium hypochlorite, asserted in 1894[1,90]

> . . . Is it desirable in any case to treat a city's water supply with a powerful disinfectant like the hypochlorites? When the question is put in this bald way I cannot think it will receive the approval of engineers and sanitarians. . . .
>
> In cases where a water supply has got into such a hopelessly bad condition that nothing will render it safe but disinfection by chloride of soda or chloride of lime, it is high time, I think, to abandon the supply and in this opinion I feel sure most water works engineers will coincide.

This, only 70 years ago, from an eminent man in the field who was not the only skeptic of what later was to revolutionize water treatment.

It was not until well in the 1890s, after Schwann, Pasteur, Koch, and others had made their invaluable contributions to the science of bacteriology, that the use of chlorine and chlorine bleaches was critically evaluated by various English, French, German, and American scientists, and that they were demonstrated as efficacious water and waste disinfectants. The investigations, rarely extending to plant-scale applications of a continuing nature, related to the effect of chlorine demand substances, chlorination and dechlorination, and contact periods required. German scientists seemed to have been more ambitious and aspired to instantaneous sterilization.[84]

The earliest recorded use of chlorine directly for water disinfection in the United States was in January, 1896, when W. M. Jewell utilized electrolytically produced chlorine gas for a week or two, in conjunction with filtration studies by G. W. Fuller, at the Louisville, Kentucky, Experimental Station.[91] (In 1909, Jewell again experimented with chlorine gas, and later chlorinated lime, for temporary treatment of filter effluents at Adrian, Michigan.)[92] In that same year a typhoid epidemic on the Adriatic Sea was arrested by the application of bleaching powder to the water supply, excess chlorine being neutralized by sodium sulfite.[1] In 1897 Sims Woodhead in England used bleach solutions as a temporary measure to sterilize potable-water distribution mains at Maidstone, Kent, subsequent to a typhoid fever epidemic.[93] All these, however, were only temporary applications.

There appears to be agreement that chlorination of water as a continuous treatment process was first adopted at Middlekerke, Belgium, in 1902, when Dr. Maurice Duyk introduced chlorinated lime and perchloride of iron to raw water prior to sand filtration. Continued until 1921, this "Ferrochlor" process had the dual objective of aiding coagulation and making the water bacteriologically safe.[94,95] In 1903, studies of the destruction of pathogens by chlorine compounds were described by Lieutenant Nesfield of the British Indian Army Medical Service, who also suggested their application to prevent waterborne-disease transmission among military personnel. The report of these studies is especially interesting from a historical standpoint because it contains the first suggestion of the possibilities of compressed chlorine gas in lead-lined iron cylinders.[96]

The second continuous municipal application of chlorine to water is considered to have been in England at the Lincoln filter plant. There, from 1904 to 1905, Sir Alexander Houston and Dr. McGowan employed a sodium hypochlorite solution ("Chlorous," containing 10 to 15 per cent available chlorine) in an effort to combat an epidemic of typhoid.[84,97,98]

In North America, the first continuous municipal application of chlorine to water was made in 1908 when J. L. Leal and G. A. Johnson used sodium hypochlorite to disinfect the 40-mgd Boonton reservoir supply of the Jersey City, New Jersey, Water Works.[84,99–102] The adoption of chloride of lime disinfection the next year at Poughkeepsie, New York,[103] of electrolytically produced sodium hypochlorite at Philadelphia, Pennsylvania,[104] and elsewhere, all following court recognition and acceptance of the practice as a public health safeguard,[105,106] paved the way for rapid extension of disinfection of public water supplies.

During the infancy of water chlorination, the only commercial sources of chlorine were chlorinated lime (also termed "chloride of lime," "bleaching powder," etc.) and sodium hypochlorite bleach solutions. The poor stability and variable effective chlorine content of these materials caused many operating difficulties, and often inadequate disinfection dosages were used. Moreover, equipment feeders then available yielded erratic results. But in 1909, liquid chlorine in steel containers became commercially available. The following year Maj. C. R. Darnall of the U.S. Army Medical Corps experimentally employed it for water disinfection at Fort Myer, Virginia, using a dry gas chlorine feeder of his own design, which was later patented.[85,107]

The first full-scale use of liquid chlorine for water disinfection followed in 1912 when E. E. Gillick and H. F. Huy successfully eliminated a recurring typhoid outbreak at Niagara Falls, New York, using solution-feed equipment developed by Dr. Georg Ornstein. Other applications promptly followed at Wilmington, Delaware, and Philadelphia, Pennsylvania.[85,108–111] In 1913 improved equipment invented by C. F. Wallace and M. F. Tiernan to measure chlorine gas, dissolve it in water, and apply the solution was installed at Boonton, New Jersey, replacing the use of sodium hypochlorite. These developments paved the way for the further extension of water disinfection and the use of liquid chlorine for that purpose.

Hypochlorite water chlorination gradually decreased in popularity, but it received renewed stimulus with the commercial availability, in 1928, of high-test calcium hypochlorite, a more stable and active material than the various bleaching powders previously available.

EVOLUTION OF WATER CHLORINATION PROCESSES

Simple Chlorination. In its initial applications, chlorination was a final adjunct to filtration and other existing water purification processes or, in some instances, it was the only treatment provided. Very soon, however, advocates of chlorination began to recognize the usefulness of chlorine for other purposes in addition to disinfection and pioneered extended water-treatment applications. In 1914, prechlorination (application of chlorine ahead of filtration) was introduced as an aid to coagulation at Exeter, New Hampshire.[112] During World War I it was adopted by Sir Alexander Houston in London as a substitute for prolonged water storage. In 1921, largely as a result of the research findings of R. S. Weston and N. J. Howard, it was adopted at Toronto, Ontario.[113,114] It was not until about 1927, however, that the practice received much recognition in the United States.

Chlorine and Ammonia Treatment. The influence of ammonia on the disinfecting capacity of chlorine (hypochlorites) was observed by S. Rideal; he noted that during the chlorination of sewage, bactericidal action continued even after all free chlorine or hypochlorite had disappeared.[84,116] Sir Alexander Houston also recognized the superior advantages of chloramine in some instances and suggested the application of ammonia prior to chlorine to avoid tastes resulting from reactions of chlorine with organic material.[112] In Canada, Joseph Race conducted a series of experiments from 1915 to 1917 on the relative bactericidal efficiency of hypochlorites and observed the elimination of aftergrowths, which he attributed to the germicidal capacity of chloramines; in 1917, the chlorine-ammonia process was adopted at Ottawa on a plant-scale basis.[85,114] In the United States the use of chloramines had been successfully adopted at Denver, Colorado, for this purpose in 1916.[84] Later McAmis[112,115,117] successfully used liquid chlorine and anhydrous ammonia to prevent the formation of chlorphenol tastes resulting from contact of residual chlorine with the linings of mains or the painted interior walls of standpipes. Subsequently, the process was studied by Spaulding at Springfield, Illinois, and by Braidech in 1929 at Cleveland, Ohio.[112,113] The widespread adoption of chlorine-ammonia treatment followed recognition that the combination of chlorine and ammonia provided a more stable disinfecting residual than that provided by chlorine alone, and that these materials could be applied to limit the development of objectionable tastes.[118] Chlorine-ammonia treatment later declined in popularity, largely due to the advent and development of "free residual chlorination" processes and the realization of the superior bactericidal efficiency of hypochlorous acid. (Currently the principal application is postammoniation to provide long-lasting chloramine residuals in potable-water distribution systems.)

Superchlorination and Dechlorination. Experimental treatment for taste and odor destruction through oxidation by excess chlorine followed by dechlorination was reported as early as 1912 and again in 1916 by Sir Alexander Houston.[112,119] It was he who proposed the terms "superchlorination" and "dechlorination" and who demonstrated, in 1925, that the more chlorine added, the more certain is the absence of taste after dechlorination. N. J. Howard and R. E. Thompson had reached a similar conclusion in 1922 and brought the superchlorination-dechlorination concept to ultimate fruition in 1926 with their successful application of the process to eliminate chlorphenol tastes at the 70-mgd Toronto filter plant.[113,114] Shortly thereafter, C. R. Cox and F. E. Hale[120] also reported application of the process in New York, primarily for destruction of tastes due to algae.

Breakpoint Chlorination. The "breakpoint" concept of water chlorination began to emerge in 1939 when Faber[121] and Griffin[122] reported that some waters exhibit a break in the chlorine residual curve if a sufficient amount of chlorine is applied to the water and the contact time is adequate. It was further developed in 1940 when H. A. Brown at Ottumwa, Iowa,[123] demonstrated plant-scale applicability, and C. K. Calvert[124,125] demonstrated the fundamentals of chlorine-ammonia reactions and the existence of free chlorine in water after all ammonia has been destroyed by chlorine. Impetus for the adoption of breakpoint chlorination was soon thereafter provided by P. C. Laux's demonstration[126,127] that free chlorine alone is present when full color develops instantly in the orthotolidine colorometric test for residual chlorine. Various test procedures for distinguishing between free and combined chlorine were subsequently introduced and perfected, mostly during the 1940s and in later years.

Chlorine Dioxide. As early as about 1900 the use of chlorine dioxide for water disinfection had been tried experimentally, but practical application proved unfeasible because of the instability of the gaseous material and of the necessity of on-the-spot generation. At about the time breakpoint chlorination was introduced, sodium chlorite was commercially developed as a bleaching agent. A dry flaked or powdered material that is readily soluble in water, it readily reacts with chlorine to produce an aqueous solution of chlorine dioxide. The method soon thereafter was experimentally employed and finally adopted on a full-scale basis at Niagara Falls, New York, in 1944 for control of phenolic tastes and odors.[128] (Chlorine dioxide oxidizes phenols without formation of odorous intermediate products.)

Although the bactericidal properties of chlorine dioxide apparently are about equal to those of chlorine, it is rarely applied solely for the purpose of disinfection. Cost and the lack of a satisfactory differential residual test at low concentrations normally maintained in water treatment doubtless contribute to this present condition. The literature contains several reports, however, of successful applications for oxidation of iron, manganese, and phenolic and chlorphenolic compounds for control of certain algae, and for control of taste and odor problems in general.[129]

Process Control. Improvements in chlorine disinfection materials and feeders substantially contributed to the popularity and widespread adoption of water chlorination. Disinfection dosages originally were based largely on the application of fixed amounts of chlorine. Soon it became apparent that this practice made no provision for the effects of variations in water quality and fluctuations in chlorine demand. Gradually, the concept of varying chlorine dosage on the basis of residual chlorine was established, and iodometric methods for qualitative and quantitative assay of residual chlorine were developed. The use of orthotolidine as a qualitative indicator of residual chlorine was proposed in 1909 by E. G. Phelps,[106,110] subsequently evaluated by Kinnicut and F. W. Jones,[112] and in 1913 extended quantitatively by J. W. Elms and S. J. Houser,[130] who also developed colorimetric standards for its use. Chlorine disinfection finally was established on a scientific basis in the period from 1917 to 1919 by the work of Abel Wolman and L. H. Enslow,[131] who demonstrated the suitability and reliability of the orthotolidine test for even the smallest water supplies and recommended that water be chlorinated to the extent that some residual chlorine remain after treatment. In 1940, P. C. Laux[126,127] proposed a workable "flash" test for the qualitative determination of free chlorine to control breakpoint chlorination. Since then, a better understanding of water chlorination processes has brought many refinements in the test and suggestions of some other tests,[132,133] notably the orthotolidine-arsenite colorimetric test developed in 1944 by F. J. Hallinan and F. W. Gilcreas[134,135] to distinguish various forms of residual chlorine; the amperometric differential titration suggested in 1942 by H. C. Marks and J. R. Glass;[136] A. T. Palin's various differential tests for available chlorine;[137–139] and methods applicable to chlorine dioxide.[140,141]

Current Status. The past half-century of experiment, development, and refinement has crystallized certain practices and control procedures to ensure effectiveness of chlorine for disinfection and other treatment applications. No other community water-treatment process enjoys such popularity and almost universal adoption, particularly in the United States.[142] Certainly not all of the public health protection and disease prevention afforded by current water-treatment technology can be attributed to chlorination, but its value, as evidenced by its development, is suggested in Table 5–2.

In 1963, the latest year for which United States statistics are available at this writing, more than half of all existing United States water-treatment facilities employed chlorination as the only treatment. Moreover, about 90 per cent of the existing facilities employing some form of treatment used chlorine for disinfection or in conjunction with other water-treatment processes and served more than 134 million persons. These facilities represented about 89 per cent of the United States population served by all community water systems, both treated and untreated, and about 96 per cent of the United States population served with treated water.

It is estimated that in 1960 more than 80,000 tons of liquid chlorine were used in the United States for disinfection and other treatment of community and industrial water supplies; in Canada about 5,000 tons were used. Although liquid chlorine surpasses hypochlorites for these purposes, particularly at larger facilities, hypochlorite chlorine forms are by no means obsolete or diminishing in importance. For the period from 1948 to 1958 the number of United States facilities using liquid chlorine increased by about 40 per cent, while the number using hypochlorites increased by almost 100 per cent. This undoubtedly is due to the adoption of chlorine disinfection at small treatment plants where hypochlorites are especially appropriate.

Liquid chlorine is the least expensive form of chlorine that can be employed where material requirements are substantial. In small waterworks installations and for emergency or specialized uses some chlorine-containing materials might be more satisfactory and economical. Among such materials are the various hypochlorites, chlorinated lime, chlorine dioxide (released from sodium chlorite, $NaClO_2$), and chloramines produced from the purposeful combination of chlorine with ammonia or other nitrogenous material.

Within the past decade or two the functional advantage of treatment employing amounts of chlorine greater than those formerly considered

TABLE 5-2 Summary of Growth of U.S. Water-treatment Facilities Using Chlorine*[143–145]

Year	Number of facilities				Forms employed					Population served (10^6) by facilities chlorinating
	Total treating	Using chlorine								
		Number	Per cent of total treating	Per cent increase	Hypochlorites	Gas	Both	Chlorine-ammonia	Misc. or unknown	
1910	....	18	...	.....	.....	.....	....	....	....	1.18 +
1915	....	340	...	1,790	.....	.....	....	....	....	15.58
1930	....	2,917	...	755	.....	.....	....	....	....	?
1940	....	4,650	...	60	728	2,563	?	668	683	63.50(est.)
1948	6,986	6,137	88	32	1,557	3,613	37	702	226	80.63
1958	9,911	8,845	89	45	3,029	5,118	157	404	137	117.32
1962†	?	10,405	...	.....	3,873	5,929	202	308	?	134.07

*Data are not strictly comparable due to variations in statistical reporting and analytical procedures. 1958 and 1962 data include Alaska, Hawaii, Puerto Rico, and the Virgin Islands.

†Unpublished Public Health Service data.

adequate has been clearly appreciated. The wider adoption of continuous chlorine treatment may be expected to continue to develop inasmuch as high-rate chlorination provides a means of achieving high standards of bacteriological quality and of improving operation of other water-treatment processes. Besides its continuous application as an integral part of potable-water treatment, a number of other specialized applications of chlorine have been proven. Principal among such applications is the disinfection of new or repaired pipelines, tanks, and reservoirs; in fact, practically all states require that all new or repaired sections of potable-water distribution systems be suitably chlorinated before being put into service.

Although bathing waters have not been epidemiologically implicated in the transmission of respiratory, dermatological, and gastrointestinal disorders often associated with bathing in polluted waters, most health authorities maintain that sanitary conditions exist only when there is provided and maintained at all times an active disinfectant in sufficient concentration to effect prompt and continuous pollution control. By far, chlorine in its various forms, including the newer, more stable organic chlorinated cyanurics, is the disinfectant most widely recommended and used for this purpose.

Bathing water chlorination does not differ greatly from drinking water chlorination except that in addition to the destruction of pathogenic organisms, the control of algae and destruction of organisms of sanitary importance that are casually or deliberately introduced by bathers is indicated. Continuous chlorination during filtration and recirculation of pool water is generally needed for larger pools, and intermittent treatment usually is considered makeshift and suitable only for smaller, private pools. (Chlorine-ammonia treatment for pool disinfection has declined in popularity in recent years, and free-residual practice is becoming more widespread in many parts of the United States. Customary treatment involves maintenance of a free available chlorine residual of 0.5 to 1.0 mg/l except where breakpoint processes are employed. Combined residuals in the range of 0.7 to 1.0 mg/l, and preferably higher, usually are indicated.)

Chlorine is extensively employed in the treatment of a variety of industrial-process waters. Probably the greatest single uses are for the control of bacteria, algae, slime, and macroscopic biological fouling organisms in fresh and saline condenser cooling waters, and in the pulp, paper, and beverage, canning, and other food processing industries. Chlorination treatment in such applications may be continuous or intermittent and may be even more exacting than for potable-water supplies. Alteration of the chemical character of some industrial-process waters frequently is accomplished by chlorine. Such applications include sulfur dioxide and ammonia destruction, iron and manganese reduction (brewing, beverage, paper, textile, laundering, and photographic processing), color reduction (textile and paper-pulping bleaching operations), and oxidation of organics (chemical and food processing industries).

PRINCIPLES OF WATER CHLORINATION

Treatment Objectives. Chlorine is used in water treatment (1) for disinfection, to destroy or attenuate microorganisms of sanitary significance; (2) for oxidation, to purposely modify the chemical character of the water to which it is applied; or (3) for both disinfection and oxidation. Actually, the toxic character of chlorine and some of its compounds is attributable in large measure to their oxidizing capacity, but oxidizing capacity is not necessarily a measure of germicidal efficiency.[146]

Disinfection is the principal and most common objective of chlorination. In fact, the terms "disinfection" and "chlorination" largely have come to imply the same treatment, even though chlorine might be specifically utilized alone or as an integral part of other treatment to accomplish or enhance objectives other than disinfection. As later discussed, not all chlorine forms or reaction products are equally effective or applicable for disinfection and/or oxidation reactions.

Water chlorination has evolved from a relatively crude process application to a highly efficient one. This is attributable largely to improved methods of testing the effectiveness of treatment and through these improved definition of the biological and chemical processes involved.

Oxidation-reduction Potentials. Chlorine and chlorine-containing compounds are potent oxidizers and can be dissipated in reactions with a variety of inorganic and organic materials in water before significant disinfection is accomplished. Both the range and rate of reactions complicate the use of chlorine for disinfection, especially if the water to be treated is heavily polluted. The oxidation-reduction (redox) potential can be considered a measure of the tendency chlorine has to react with other materials, but it provides no indication of the rate of reactions or the speed at which they will occur. As a general rule, chlorine reacts with fewer materials as the pH increases, and with those materials with which it reacts the reaction rate increases with increasing temperatures.

The oxidation reactions of chlorine with inorganic reducing substances such as sulfides, sulfites, ferrous iron, and nitrites generally are very rapid. Some dissolved organic materials also react with chlorine rapidly, but the time required to complete most reactions of chlorine with organics usually is considered a matter of hours. The kinetics of the reactions of chlorine with ammonia, amino acids, and proteins and the products produced by these reactions have been extensively studied[46,121–125,144–149] and are highlighted on p. 188.

Listed in Table 5–3 are representative redox potentials[4,150] for various

TABLE 5-3 Redox Potentials of Chlorine and Other Oxidation-reduction Reactions

Substance	Reaction	Potential, volts
Hypochlorous acid	$HOCl + H^+ + 2e^- \rightarrow Cl^- + H_2O$	+1.49
Chlorine gas	$Cl_2 + 2e^- \rightarrow 2\,Cl^-$	+1.36
Hypochlorite ion	$ClO^- + 2\,H_2O + 2e^- \rightarrow Cl^- + 2(OH)^-$	+0.94 +1.2 at pH 7
Chlorine dioxide	$ClO_2 + e^- \rightarrow ClO_2^-$	+1.5
Chlorite	$ClO_2^- + 2\,H_2O + 4e^- \rightarrow 2\,Cl^- + 4(OH)^-$	+0.79 at pH 4 +0.66 at pH 9
Iodine	$I_2 + 2e^- \rightarrow 2\,I_2$	+0.54
Bromine	$Br_2 + 2e^- \rightarrow 2\,Br^-$	+1.09

chlorine and other oxidation-reduction reactions (there exist minor variations among different reference sources).

The magnitude of redox potentials listed is a measure of the driving force behind the reaction or its tendency to completion, but provides no clue as to the rate at which it proceeds.

Reactions with Water. When chlorine is added to chemically pure water, a mixture of hypochlorous (HOCl) and hydrochloric (HCl) acids is formed:

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^- \qquad (2)$$

At ordinary water temperatures this reaction is essentially complete within a few seconds. In dilute solution and at pH levels above about 4, the equilibrium shown in Eq. (2) is displaced to the right, and very little Cl_2 exists in solution. In normal practice (excepting the concentrate from solution-feed chlorinators), the amount of chlorine supplied to water does not produce a concentrated solution of such strength as to yield such a low pH. The oxidizing property of the chlorine is, however, retained in the HOCl formed, and it is also in this form that the principal disinfecting action of chlorine solutions is associated.

Hypochlorous acid ionizes or dissociates, a practically instantaneous reaction, into hydrogen and hypochlorite ions (note that the reaction is reversible), the degree of dissociation depending on pH and temperature:

$$HOCl \rightleftharpoons H^+ + OCl^- \qquad (3)$$

Hypochlorous acid is weak and dissociates poorly at pH levels below about 6; thus, chlorine exists predominantly as HOCl at low pH levels. Between a pH of 6.0 and 8.5, there occurs a very sharp change from undissociated HOCl to almost complete dissociation. At 20°C above a pH of about 7.5 and at 0°C above a pH of about 7.8, hypochlorite ions (OCl^-) predominate, and they exist almost exclusively at levels of pH around 9.5 and above (see Fig. 2). The pH of chlorinated water supplies is normally within the range where chlorine may exist both as hypochlorous acid and hypochlorite ion. *Chlorine existing in water as hypochlorous acid and hypochlorite ions is defined as free available chlorine.*

Hypochlorite chlorine forms, such as high-test (70 per cent available chlorine) calcium hypochlorite, $Ca(OCl)_2$, and sodium hypochlorite, NaOCl, ionize in water and also yield hypochlorite ions:

$$Ca(OCl)_2 + H_2O \rightleftharpoons Ca^{++} + 2OCl^- + H_2O \tag{4}$$

$$NaOCl + H_2O \rightleftharpoons Na^+ \; OCl^- + H_2O \tag{5}$$

The hypochlorite ions also establish equilibrium with hydrogen ions, depending on the pH, as shown by Eq. (3). Thus, the same equilibria are established in water regardless of whether elemental chlorine or hypochlorites are employed. The important distinction is the resultant pH and, hence, the relative amounts of HOCl and OCl^- existing at equilibrium. Chlorine tends to decrease the initial pH, and hypochlorites tend to increase it.

From Eq. (2), it is evident that the hypochlorous and hypochlorite acids

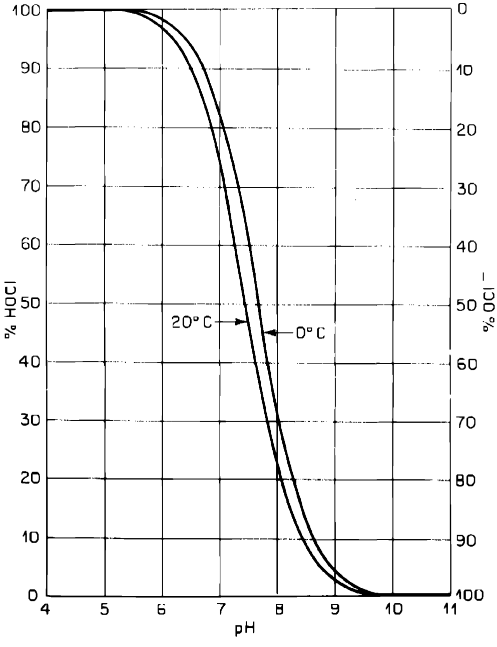

Fig. 2 Distribution of HOCl and OCl^- in water at indicated pH levels.[146]

produced tend to lower pH and reduce alkalinity. Each part of chlorine added will neutralize not less than 0.7 parts of alkalinity (as $CaCO_3$) and may neutralize 1.4 parts, depending upon the extent to which HOCl is ionized and the manner in which chlorine is consumed by substances in the water. Hardness-producing materials, principally the carbonates and bicarbonates of Ca and Mg, tend to buffer water against significant changes in pH that otherwise would accompany the addition of small amounts of acid or alkaline materials. If sufficient amounts of chlorine are applied to deplete natural alkalinity to such an extent that the pH is substantially decreased, however, pH correction may be indicated as auxiliary treatment. Hypochlorites always contain excess alkali for stability and tend to raise pH levels, but usually by insignificant amounts.

Chlorine-Ammonia Reactions. The reactions of chlorine with ammonia are of great significance in water chlorination processes, especially disinfection. As previously noted the kinetics of these reactions have been extensively studied. When chlorine is added to water containing natural or added ammonia (ammonium ion exists in equilibrium with ammonia and hydrogen ions), the ammonia reacts with HOCl to form various chloramines which, like HOCl, retain the oxidizing power of the chlorine.[121–125] The reactions between chlorine and ammonia may be simply represented by:

$$\underset{\text{Monochloramine}}{NH_3 + HOCl \rightarrow NH_2Cl + H_2O} \qquad (6)$$

$$\underset{\text{Dichloramine}}{NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O} \qquad (7)$$

$$\underset{\text{Trichloramine or nitrogen trichloride}}{NHCl_2 + HOCl \rightarrow NCl_3 + H_2O} \qquad (8)$$

The distribution of the reaction products is governed by the rates of formation of monochloramine and dichloramine which are dependent upon pH, temperature, time, and initial $Cl_2:NH_3$ ratio.[146,147] In general high $Cl_2:NH_3$ ratios, low temperatures, and low pH levels favor dichloramine formation. Figure 4 illustrates the relative amounts of monochloramine and dichloramine likely to be formed at various pH levels when the $Cl_2:NH_3$ ratio is equimolar (5:1 on a weight basis). Although reported data differ in some degree, it is evident that some dichloramine can be anticipated at pH levels below 7. Palin's work[147,148] further suggests that at pH levels below about 7.5, some nitrogen trichloride can be anticipated. Dependent on a number of factors, such as the free ammonia and organic nitrogen content of the raw water, the level of free residual chlorination applied, contact time, pH, type of water plant, etc., nitrogen trichloride can pose a considerable problem which may be disposed of by various means. The subject is a complex one and has been extensively treated elsewhere.[151–153]

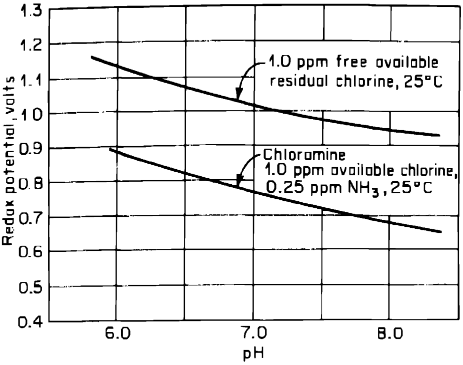

Fig. 3 Variation of redox potential of solutions containing different chlorine compounds.[130]

Chlorine also reacts with organic nitrogenous materials, such as proteins and amino acids, to form organic chloramine complexes. *Chlorine existing in water in chemical combination with ammonia or organic nitrogen compounds is defined as combined available chlorine.*

The oxidizing capacity of free chlorine solutions varies with pH because of variations in the resultant $HOCl:OCl^-$ ratios. As shown in Fig. 3, the redox potential decreases at high pH levels where OCl^- predominates. This applies also in the case of chloramine solutions as a result of varying $NHCl_2:NH_2Cl$ ratios, and where monochloramine predominates at high pH levels. The redox potential of the chloramines is much lower than that of free available chlorine, indicating that the ammonia chloramines also are less reactive than free available chlorine.

Other Chlorine Reactions. The reaction between hydrogen sulfide and chlorine, generally very rapid, is typical of that which occurs with inorganic reducing materials:

$$H_2S + 4\ Cl_2 + 4\ H_2 \rightarrow H_2SO_4 + 8\ HCl \qquad (9)$$

In the reduced form of a chloride ion, Cl^-, oxidizing power does not exist. One part of H_2S theoretically can be oxidized by about 8.5 parts of chlorine, and chlor-oxidation treatment sometimes is practiced with this objective in mind. About 10 parts of alkalinity (as $CaCO_3$) are consumed by the reaction which occurs optimally at a pH of about 9.

Iron and manganese in water also affect chlorination practices; if the pH is high enough for hydroxide formation, and if sufficient chlorine is added, ferrous and manganous forms of the metal will be rapidly oxidized to insoluble hydroxide forms. Chloramines do not enter vigorously into these oxidation reactions. For satisfactory manganous oxidation, free available

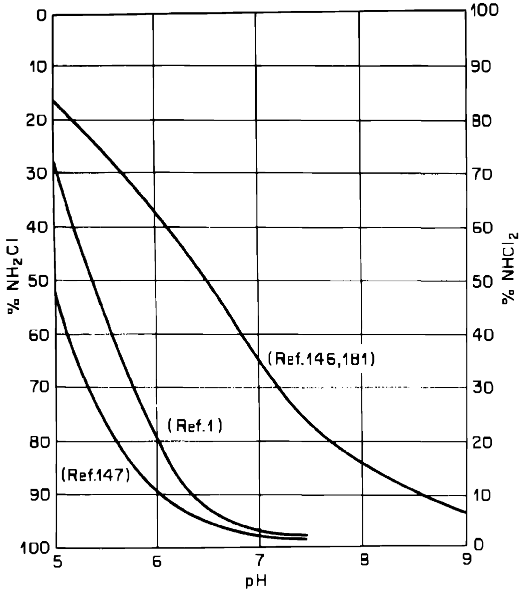

Fig. 4 Distribution of chloramines in 25 °C water at indicated pH levels and Cl_2:NH_3 (as N), weight ratio = 5:1.

chlorine, as distinct from combined available chlorine, is required. For iron removal the optimum pH is 7 or above, and for manganese removal the optimum pH is 10. About 0.6 and 1.3 parts of chlorine are required, respectively, for each part of Fe and Mn removed, and about 0.9, and 3.4 parts of alkalinity (as $CaCO_3$) are consumed.

Nitrites are occasionally present in some waters, particularly those contaminated by sewage and certain industrial wastes. They, too, are readily oxidized to nitrates by chlorine, particularly free available chlorine, each part of nitrite consuming about 1.5 parts of chlorine.

A few organic reducing materials may be present in potable waters but their concentration usually is low. However, there are a variety of chlorine-reactive, organic materials in some waters that can exert a substantial influence on chlorine requirements, depending upon available chlorine concentration and reaction time. Some dissolved organic materials react with chlorine rapidly, but, generally, the time required for the completion of most organic reactions is a matter of hours. Under some conditions, chlor-addition or chlor-substitution products might be formed, while under others the organic material may be completely oxidized. (Organic chlorine complexes generally have low bactericidal capacity and are of principal concern in water chlorination practice because of the chlorine consumed and the tastes and odors they may impart.)

"Available Chlorine." Equation (2) illustrates the reaction of chlorine and water to form a weak solution of hypochlorous and hydrochloric acids. The chlorine atom of the HOCl may be considered positive (valence is plus 1) and is the "active" chlorine referred to in disinfection literature. As the equation demonstrates, only half of the chlorine is utilized in the formation of HOCl. As illustrated in Eqs. (4) through (8), all the chlorine in hypochlorites and chloramines is utilized in the formation of HOCl.

The term "available chlorine content" was established in the early days of chlorination as a basis of comparison of the potential disinfecting power of chlorine compounds with that of elemental chlorine, at a time when it was believed that the gas was 100 per cent utilized or "available" in disinfection reactions. The available chlorine content of a solution is determined by titrating the iodine which the solution will liberate from an acidified iodide solution. See Eq. (20). The calculated weight of elemental chlorine, Cl_2, required to liberate the same amount of iodine is the "available chlorine content" of the solution. [Because only half of the Cl_2 molecule is positive in solution, the available chlorine content of hypochlorites and chloramines is just twice the "active" (positive) chlorine content. For example, the percentage of chlorine in dichloramine is 82.5, but the available chlorine content is 165.0 per cent.] Thus, the titration described is a quantitative measure of the oxidizing power of a solution, determined by the ability of the solution to release iodine from acidified iodide, and expressed in terms of elemental chlorine. The oxidizing power of materials containing no chlorine can be expressed in terms of available chlorine. Anhydrous hydrogen peroxide, for example, has an equivalent available chlorine content of 208 per cent. It should be noted, however, that the oxidizing power of a material is not necessarily a measure of its disinfecting efficiency; thus, hydrogen peroxide is a powerful oxidant but a poor water disinfectant.

The per cent available chlorine of various chlorine-containing materials is indicated in Table 5-4.[153]

Mode of Disinfecting Action. Chlorine disinfection involves a very complex series of events and is influenced by the kind and extent of reactions with chlorine-reactive materials (including nitrogen), temperature, pH, the viability of test organisms, and numerous other factors. Such factors greatly complicate attempts to determine the precise mode of action of chlorine on bacteria and other microorganisms. Over the years several theories have been advanced. One early theory held that the action of chlorine reacts directly with water to produce nascent oxygen; another held that the action of chlorine is due to complete oxidative destruction of organisms. These were nullified because small concentrations of hypochlorous acid were observed to destroy bacteria whereas other oxidants (such as hydrogen peroxide or potassium permanganate) failed to do like-

TABLE 5-4 Per Cent Available Chlorine of Various Chlorine Materials

Material	Available chlorine, %
Cl_2, chlorine	100 (by definition)
Bleaching powder (chloride of lime, etc.)	35–37
$Ca(OCl)_2$, calcium hypochlorite	99.2
Commercial preparations	70–74
$NaOCl$, sodium hypochlorite (unstable)	95.2
Commercial bleach (industrial)	12–15
Commercial bleach (household)	3–5
ClO_2, chlorine dioxide	263.0
NH_2Cl, monochloramine	137.9
$NHCl_2$, dichloramine	165.0
NCl_3, nitrogen trichloride	176.7
$HOOCC_6H_4SO_2NCl_2$ (Halazone)	52.4
NClCONClCONCl CO trichloroisocyanuric acid	91.5
CONClCONClCONH dichloroisocyanuric acid	71.7
CONClCONClCON Na sodium dichloroisocyanurate	64.5

SOURCE: W. H. Sheltmire, Chlorinated Bleaches and Sanitizing Agents, Chap. 17 of ACS Monograph "Chlorine," Reinhold Publishing Corporation, New York, 1962.

wise. A later theory suggested that chlorine reacts with protein and amino acids of cells to alter and ultimately destroy cell protoplasm. Currently it is considered that the bactericidal action of chlorine is physiochemical, but among yet-unanswered questions are those pertaining to phenomena such as variations in resistance of bacteria, spores, cysts, and viruses; the appearance of mutants; etc.

Green and Stumpf[154] suggested in 1946 that death of bacterial cells results from a chemical reaction of HOCl with an enzyme system (possibly on especially sensitive triosephosphate dehydrogenase, although not excluding others) essential to glucose oxidation and cellular metabolic activity. (The reactions are presumed to involve irreversible HOCl oxidation of sulfhydryl-containing enzymes, and the investigations by Ingols et al.[155] appear to substantiate this.) These authors suggested that spores were inactivated by a method different from that applicable to vegetative cells, having observed that spore survival is not dependent upon the ability of chlorine to oxidize glucose. Because survival of spores is determined by their ability to form vegetative cells, it was postulated that spores subjected to chlorine retain ability to produce more of the susceptible enzyme, while vegetative cells lose ability for enzyme regeneration. (Most viruses do not have demonstrable enzymes and yet are inactivated by chlorine.) It has been suggested that the phenomenon of unbalanced growth can be the effective mechanism of death for microorganisms. Wyss[156] has noted that convincing evidence exists that destruction of part of an enzyme system throws the cell out of balance so that by progress of its own metabolism it dies before cell functions can be brought back in balance.

While the enzyme-deactivation theory does provide an explanation of the extreme sensitivity of certain organisms to chlorine, it does not furnish the complete answer, for enzymes removed from cells are equally susceptible to attack by some oxidants other than chlorine, whereas chlorine is markedly superior to these same oxidants in attacking intact cells. Fair et al.[146] suggested that the difference might be explained on the basis that not only is the ability of a disinfectant to react on a key enzyme system important, but also its ability to penetrate the cell. The rate of diffusion of the disinfectant into the cell largely determines the rate of disinfection and relative efficiencies of disinfecting agents. Thus, perhaps the superior effectiveness of HOCl to other chlorine forms is due not to its strong oxidizing power, but rather to its small molecular size and electrical neutrality which allow it to readily penetrate the cell. Hypochlorite ion has little if any bactericidal effect, and its negative charge is presumed to impede cell penetration. The greater resistance of spores compared with vegetative cells, then, might well be due to the permeability barrier which is not readily penetrated by such compounds as chlorine or its derivatives. Confirmation of these various theories must be sought in more extensive fundamental studies of the mechanism and rate of kill of organisms by various disinfectants and of variations in these with changing and variable environmental factors.

Marks et al.,[157] in studying factors affecting the bactericidal action of nitrogen-containing (chloramine) chlorine compounds, noted that observed variations in death rate are attributable to the extent of hydrolysis and that unhydrolyzed chloramines also exhibit bactericidal properties. The hydrolysis equilibrium of the chloramine determines the concentration of hypochlorous acid that is present. The small hydrolysis constants of chloramines, especially those organic in nature, permit only a small amount of hypochlorous acid formation initially, but as the HOCl is depleted more is supplied by continuous hydrolysis of the chloramine. The hydrolysis constant of monochloramine is too low for hypochlorous acid to be formed in significant amounts; dichloramine has a higher hydrolysis constant and therefore provides more effective disinfection. Organic chloramines also have different hydrolysis constants and, accordingly, different disinfecting capacities; some may be more effective than monochloramine and dichloramine, while others may be bacteriostatic rather than bactericidal.[153] Hydrolysis generally is greater as pH increases but, simultaneously, HOCl becomes more ionized to the inactive OCl^-. Thus, pH has a significant effect on the activity of HOCl and various chloramines. Additionally, each of the several unhydrolyzed chloramines that can form by the reaction of chlorine with nitrogenous material has its own specific rate of killing microorganisms, depending on the nature of the compound and the ratio of nitrogen to chlorine in the reaction mixture.

Studies reported by Ingols et al.[155] indicate that monochloramine, unlike hypochlorous acid, fails to immediately labilize sulfhydryl radicals to an irreversible form, and suggest that other enzyme systems might be affected and that monochloramine might well be bacteriostatic and not bactericidal. Further studies [158] indicate that monochloramine resembles organic chloramines in its capacity to induce chromosome aberrations in cells at concentrations that apparently produce little evidence of tissue damage, tending to support the thesis that monochloramine might attack sites other than sensitive enzymes in bacterial cells. (No evidence has been found that hypochlorous acid induces chromosome aberrations.)

The mode of action of chlorine on viruses has been only superficially investigated. On the basis of evidence that oxidative changes in the sulfhydryl radical of virus protein does not alter infectivity and because chlorine can disrupt or hydrolyze peptide linkages, substitute onto the benzyne ring of tryosine, or deaminate free ammonia radicals, Ingols[159] postulates that virus destruction by hypochlorous acid is brought about by its ability to attack many sites in the virus protein molecule rather than a specific site important in the overall economy of bacterial cells.

Regardless of what the mode of action of chlorine might be, it is abundantly evident that free and combined available chlorine forms are not alike with respect to disinfecting efficiency either on the same or different microorganisms.

PRACTICES OF WATER CHLORINATION

Evolution. Early water chlorination practices (variously termed "plain chlorination," "simple chlorination," and "marginal chlorination") were applied for the purpose of disinfection. As previously noted, chlorine-ammonia treatment (previously termed "chloramination") was soon thereafter introduced to limit the development of objectionable tastes and odors often associated with marginal chlorine disinfection. Subsequently, "superchlorination" (as then practiced) was developed for the additional purpose of destroying objectionable taste- and odor-producing substances often associated with chlorine-containing organic materials. The introduction of "breakpoint chlorination" and the recognition that chlorine residuals can exist in two distinct forms established contemporary water chlorination as one of two types: *combined residual chlorination* or *free residual chlorination.*

Combined Residual Chlorination. Combined residual chlorination practice involves the application of chlorine to water to produce, with natural or added ammonia, a combined available chlorine residual and to maintain that residual through part or all of a water-treatment plant or distribution system. Combined available chlorine forms have lower oxidation potentials than free available chlorine forms and therefore are less effective as oxidants. Moreover, they also are less effective disinfectants. In fact, about 25 times as much combined available residual chlorine as free available residual chlorine is necessary to obtain equivalent bacterial kills *(S. typhosa)* under the same conditions of pH, temperature, and contact time. And about 100 times longer contact is required to obtain equivalent bacterial kills under the same conditions and for equal amounts of combined and free available chlorine residuals.[160–163]

When a combined available chlorine residual is desired, the characteristics of the water will determine how it can be accomplished: (1) if the water contains sufficient ammonia to produce with added chlorine a combined available chlorine residual of the desired magnitude, the application of chlorine alone suffices; (2) if the water contains too little or no ammonia, the addition of both chlorine and ammonia is required; (3) if the water has an existing free available chlorine residual, the addition of ammonia will convert the residual to combined available residual chlorine. A combined available chlorine residual should contain little or no free available chlorine.

The practice of combined residual chlorination is especially adaptable after filtration (posttreatment) for controlling certain algae and bacterial aftergrowths and reducing dead-end and red-water troubles in potable-water distribution systems and for providing and maintaining a stable residual throughout the system to the point of consumer use. It is frequently preceded by free residual chlorination to ensure water potability except possibly where very long contact periods are available.

Free Residual Chlorination. Free residual chlorination practice involves the application of chlorine to water to produce, either directly or through the destruction of ammonia, a free available chlorine residual and to maintain that residual through part or all of a water treatment plant or distribution system. Free available chlorine forms have higher oxidation potentials than combined available chlorine forms and therefore are more effective as oxidants. Moreover, they are also most effective disinfectants, as already noted.

When free available chlorine residual is desired, the characteristics of the water will determine how it can be accomplished: (1) if the water contains no ammonia (or other nitrogenous materials), the application of chlorine will yield a free residual; (2) if the water does contain ammonia that results in the formation of a combined available chlorine residual, this must be destroyed by applying an excess of chlorine.

With molar Cl_2:NH_3 (as N) concentrations up to 1:1 (5:1 weight basis) monochloramine and dichloramine will be formed, the relative amounts of each depending on pH and other factors as noted on p. 194. Chloramine residuals generally reach a maximum at equimolar concentrations of chlorine and ammonia. Further increases in the $Cl_2:NH_3$ ratio result in the oxidation of ammonia and reduction of chlorine. These oxidation-reduction reactions are essentially complete when two moles of chlorine have been added for each mole of ammonia present and if sufficient contact time is provided. Chloramine residuals then decline to a minimum value, the breakpoint, when the molar $Cl_2:NH_3$ ratio is about 2:1. At this point oxidation-reduction reactions are essentially complete. Further addition of chlorine produces free residual chlorine as illustrated in Fig. 5.

The mechanics and precise products of the breakpoint reactions have not been clearly established, and it is difficult to define precisely what occurs in different situations. When chlorine is added to water containing free ammonia, chloramines are formed; but as additional amounts of chlorine are applied, the chloramines form intermediate compounds and eventually are destroyed as the reaction goes to completion. Thus, the chloramines first formed may exist while ammonia is in excess, but they are decomposed when chlorine is in excess. Beyond the breakpoint, unreacted hypochlorous acid remains in solution.

Equations (10) through (13) suggest the reactions which might occur in the destruction of chloramines (the true reactions probably encompass a combination of these and others).

$$2\ NH_3 + 2\ Cl_2 \rightarrow N_2 + 6\ HCl \qquad (10)$$

$$4\ NH_2Cl + 3\ Cl_2 + H_2O \rightarrow N_2 + N_2O + 10\ HCl \qquad (11)$$

$$2\ NHCl_2 + H_2O \rightarrow N_2O + 4\ HCl \qquad (12)$$

$$HOCl + NHCl_2 + H_2O \rightarrow 2\ NO_2 + 5\ HCl \qquad (13)$$

In any event, it is likely that nitrogen, nitrous oxide, and perhaps some nitrogen trichloride are the principal gaseous products of the breakpoint reactions. In theory, the amount of chlorine required to arrive at the breakpoint (where all ammonia is oxidized) has been variously reported at between 7.6 and 15 times the ammonia nitrogen content of the water. In practice, however, due to the presence of organic and other chlorine-reactive materials, up to 25 times as much chlorine as the ammonia nitrogen content may be required to reach this point. After free residual chlorination (beyond the breakpoint), the resulting residual should consist of at least 90 per cent free available residual chlorine and should contain little combined available residual chlorine.

The rate of the breakpoint reaction is strongly dependent upon pH; it appears to be most rapid between a pH of 7 and 8 and to decrease rapidly at lower and higher pH levels. More chloramine is present in the early

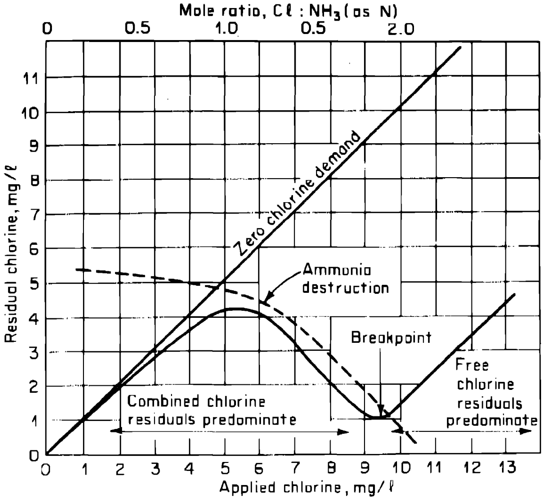

Fig. 5 Representative breakpoint chlorination curve (N = 1 mg/l).

reactions and short contact periods than in subsequent reactions and after long contact. It is, in fact, common to observe coexistence of combined and free available chlorine residuals after contact periods of 10, 20, or even 60 min. When, following breakpoint treatment, a water has a final pH of about 8 to 9, no detectable amount of nitrogen trichloride will be formed. At lower final pH levels, the amount of nitrogen trichloride can be substantial and will impart noxious odors to the water. When this form of chlorination treatment is employed, adequate contact periods must be provided, and the treated water should be exposed to air to provide for the release of gaseous products of the reactions.[119,146]

Free residual chlorination is especially suitable in the following cases:

1. Where raw water is poor
2. For oxidation of iron and manganese
3. When contact time is insufficient to accomplish disinfection by combined available forms
4. When tastes exist before treatment (also to destroy objectionable tastes and odors produced by some substances that react with chlorine and by certain algae growths)
5. To minimize biological growths on filters and to lengthen filter runs
6. To eliminate chlorine-resistant bacteria and aftergrowths in distribution systems

The practice is adaptable to prechlorination, postchlorination, and rechlorination schemes, and when chlorination is the only treatment process employed.

Waterborne Pathogenic Organisms. Experimental data are insufficient to provide a specification of the amount and kind of chlorine required for 100 per cent kill of microorganisms of sanitary significance under all conceivable combinations of each of the influencing variables already discussed. Contemporary chlorine disinfection is based on the attainment of a distinct *kind* and *amount* of residual chlorine remaining after treatment which, in turn, has been established to be adequate to ensure water potability.

Waterborne organisms of particular concern in the United States are those etiologically associated with typhoid fever, dysentery, and various gastrointestinal disorders. The causative organisms associated with most of these are of the genus *Salmonella* or *Shigella*. Diseases such as tuberculosis, anthrax, tularemia, and streptococcal or other bacterial infections in man are believed by some to be transmitted by polluted water, but firm, supporting epidemiological data are lacking. Moreover, the causative organisms do not often occur or normally survive long in water.

Chlorine disinfection operating control by testing for the presence of organisms of the coliform group is based in part on the fact that the causative bacterium of typhoid fever, *S. typhosa*, is at least as vulnerable as most coliforms, and further, that its vulnerability is fairly representative of other *Salmonella* and *Shigella* waterborne pathogens. In general, all coliform bacteria exhibit chlorine survival and resistance patterns of the same order of magnitude, even though some nonfecal coliforms, particularly *A. cloacae* and *A. aerogenes*, sometimes tend to be more resistant than *E. coli* and most commonly occurring intestinal bacterial pathogens.[167,168]

Of the protozoan diseases involving parasitic organisms that invade the body via the digestive tract, amoebic dysentery is by far the most important. Although the low incidence of this disease provides some degree of public health assurance, it is important to recognize that at concentrations normally employed by waterworks utilities, chlorine is not effective in the destruction of the causative *E. histolytica* cyst. Accordingly, the coliform standard of bacteriological safety is of no value in appraising water potability from this standpoint where chlorine disinfection is the only treatment provided.[169–172]

The enteroviruses comprise a group of organisms that multiply in the human intestine and are discharged in feces. They include three types of polio virus, at least 30 types of Coxsackie virus, and 24 types of ECHO (enteric cytopathogenic human orphan) viruses.[172] The etiological significance of the presence of such viruses in water as a result of pollutional discharge has not been fully established, yet it is important to note that present coliform indices of sanitary quality are unsuitable for ascertaining the absence of viruses from water because they are more resistant to chlorine than coliforms or other enteric bacteria.

Of all known viruses, that associated with infectious hepatitis is of greatest concern. Reports of epidemics have been recorded wherein drinking water was established as the vehicle of disease transmission; with but few exceptions, however, these have involved untreated supplies or treated supplies subsequently contaminated in the water distribution system.[173] Polio virus has frequently been mentioned as possibly being waterborne. Several epidemics of poliomyelitis attributable to water have been cited, but evidence has not been sufficiently complete to carry conviction. The possibility that polio is occasionally waterborne is not excluded, but proof is lacking.[173,174] Additionally, the adenoviruses, of which there are at least eighteen known types, make up a group of respiratory viruses that multiply in humans and are discharged in feces. No outbreaks of waterborne adenovirus infection have been documented.[173]

While there is good cause for concern over the role of waterborne viruses and chlorine-resistant organisms in disease transmission, it appears that there is insufficient conclusive evidence to justify panic over either recognized shortcomings of conventional bacteriological tests or the possible inadequacy of customary bactericidal chlorine treatment measures. It is apparent, however, that enteric viruses differ in sensitivity and resistivity to chlorine; that principal differences are among strains rather than types; that different strains are inactivated at markedly different rates; that many strains are considerably more resistant to chlorine than coliforms; that the adequacy of water treatment might not be proven by negative coliform tests; and that waterborne outbreak of some virus diseases might occur if the water is grossly polluted.[175–178]

Recently there has been considerable concern over the presence of nematodes in drinking water.[172] Free-living, nonpathogenic varieties are present especially in surface water supplies. Although they are capable of ingesting and harboring potentially dangerous organisms, they are not known to have been involved in disease transmission. From an aesthetic viewpoint, however, their presence in water is considered undesirable. Nematodes exhibit a higher resistance to chlorine than enterobacteria and enteroviruses.[179]

Minimum Bactericidal Residuals. Minimum bactericidal chlorine residuals were investigated from 1944 to 1948 by the Public Health Service. Data secured in experiments at temperatures from 20 to 25°C, using 10-min exposures to free available chlorine and 60-min exposures to combined available chlorine, are the basis for recommended minimum safe residuals illustrated in Fig. 6.[160,163] Thus, with free available residual chlorine at a pH of 6.0 to 8.0, a safe residual for complete destruction of bacteria after 10 min contact would be not less than 0.2 ppm; at a pH of 8.0 to 9.0, at least 0.4 ppm; at a pH of 9.0 to 10.0, at least 0.8 ppm; and, above a pH of 10.0, more than 1.0 ppm would be required. With combined residual chlorine at a pH of 6.0 to 7.0, a safe residual after 60 min contact would be not

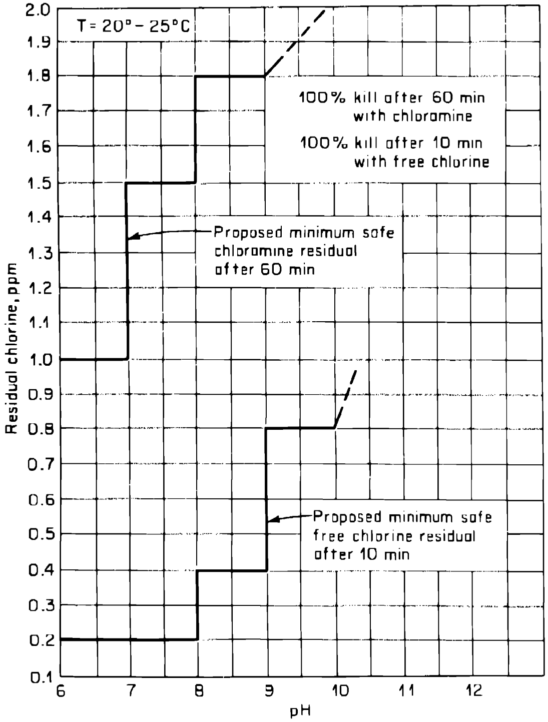

Fig. 6 Minimum free and combined bactericidal chlorine residuals.[128, 161]

less than 1.0 ppm; at a pH of 7.0 to 8.0, at least 1.5 ppm; and at 8.0 to 9.0, at least 1.8 ppm. These values are not applicable to all waters, particularly those which are turbid, nor do they apply at temperatures below 20°C.

In 1965, the National Research Council, in investigating minimum chlorine residuals applicable for military water supplies, reanalyzed the Public Health Service data and submitted recommendations based on 30 min contact.[180] As illustrated in Fig. 7, with free available residual chlorine up to a pH of about 9.2, a safe residual for complete destruction of bacteria would be not less than 0.2 ppm; at a pH of 10.0, it would be at least 0.6 ppm. A combined available residual of 2 ppm is indicated where pH is 6.8 or below, and at a pH of 10.0 more than 3 ppm might be necessary.

Minimum Cysticidal Residuals. Minimum cysticidal chlorine residuals recommended by the National Research Council[180] for military water supplies, based on the investigations by Chang, Fair, and others,[169,172] are illustrated in Figs. 8 and 9. It is significant to note that minimum chlorine requirements for cyst destruction are greater than for bacteria destruction and that diminished effect at reduced temperatures is more pronounced even under the best conditions of operation. Thus, more than 50 ppm free available residual after 30 min contact would be necessary when the pH is 8.3 and 9.5, respectively, at 2 to 5°C and 22 to 25°C. Waters containing significant amounts of organic matter or high bacterial or cyst densities would require either higher 30-min residuals or longer contact periods than those illustrated.

Viricidal and Other Residuals. Complete data are unavailable upon which to base a recommendation on residual requirements to ensure destruction of waterborne viruses.[142] From studies using human volunteers[181] it is apparent that complete control of the causative hepatitis virus depends almost entirely on the proper use of a suitable disinfectant, if it is not destroyed or inactivated by coagulation, settling, or diatomite filtration alone. According to Clarke and Chang[173] satisfactory control is obtained by prechlorinating to maintain a 0.3- to 0.4-ppm free available chlorine residual throughout treatment and 0.2- to 0.3-ppm free available residual in the plant effluent. These observers consider that the chance of survival of any human enteric virus after such treatment is remote, especially when satisfactory flocculation is employed in the treatment regimen.

Nematodes reportedly are not demobilized after 2 hr contact by a free available chlorine residual of 2½ to 3 ppm or after 1 min contact by a 15- to 45-ppm free available residual. Also, while the organisms they might have ingested might be expected to survive only a day or two, such organisms are completely protected against chlorine even when 90 per cent or more of the nematodes have been immobilized.[182] Where infested waters

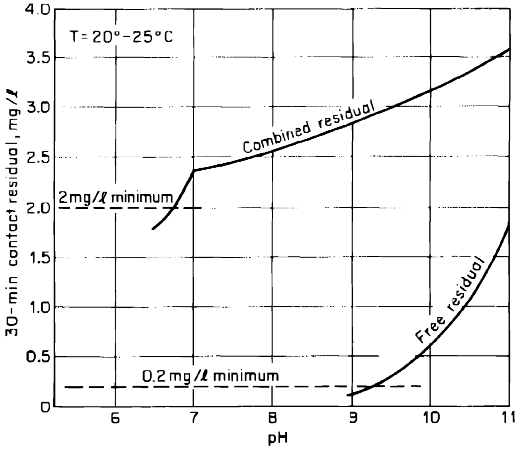

Fig. 7 Minimum free and combined bactericidal chlorine residuals.[180]

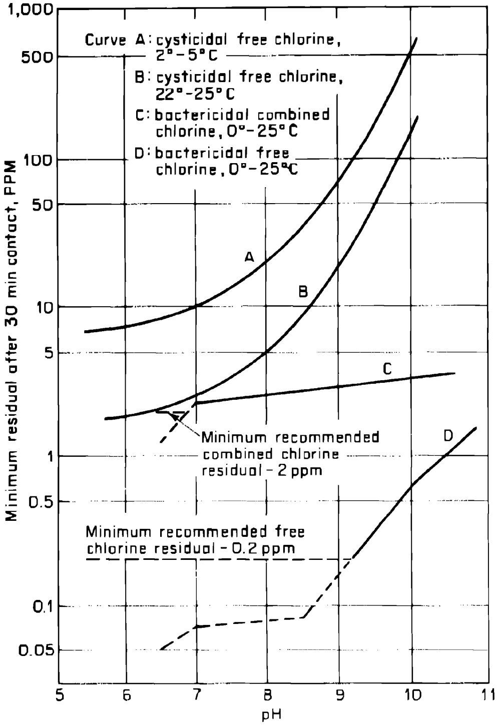

Fig. 8 Minimum free and combined bactericidal and cysticidal chlorine residuals.[180]

are a problem, it currently is recommended that supplies be prechlorinated for 6 hr to maintain a free available residual of 0.4 to 0.5 ppm; this treatment might not destroy nematodes, but it attenuates most and renders them immobile and easily removed by settling processes.

The adoption and maintenance of fixed, minimum free or combined available chlorine residuals serve only as operating guides and should not minimize, nor can they replace, cultural or microscopic analyses. Demonstration of the absence of disease-producing organisms is the only positive means of assuring safety.

Points of Application. When chlorination of water was first employed for disinfection, terminal treatment of the purification plant effluent was almost invariably practiced. Now the use of chlorine in various stages of water treatment and even in the distribution system is common practice. Multiple- or split-chlorination schemes are increasingly employed for disinfection and other purposes and frequently enhance the efficiency of many unit water-treatment processes. Fundamentally, the points at which chlorine is applied depend on the specific objectives of chlorination and on technical, practical, safety, economic, and other considerations. In practice various terms have come into common usage to specify the point and location at which chlorine is applied.

Plain or *simple chlorination* involves the application of chlorine to water that receives no other treatment. More than half of all existing water-treatment facilities in the United States fall in this category, and thus this treatment represents the sole public health safeguard. When applied to impounded or naturally elevated surface systems, chlorine usually is injected to the pipeline leading from such a gravity supply. When applied to water pumped into a system, chlorine usually is added at the pump suction using pressure beyond the pump to operate the chlorine feeders.

Prechlorination involves the application of chlorine to water prior to any other unit treatment process. Among benefits that can be achieved are: improved filter operation by reduction and equalization of the bacterial and algal load and by control of slime and mud ball formation; improved coagu-

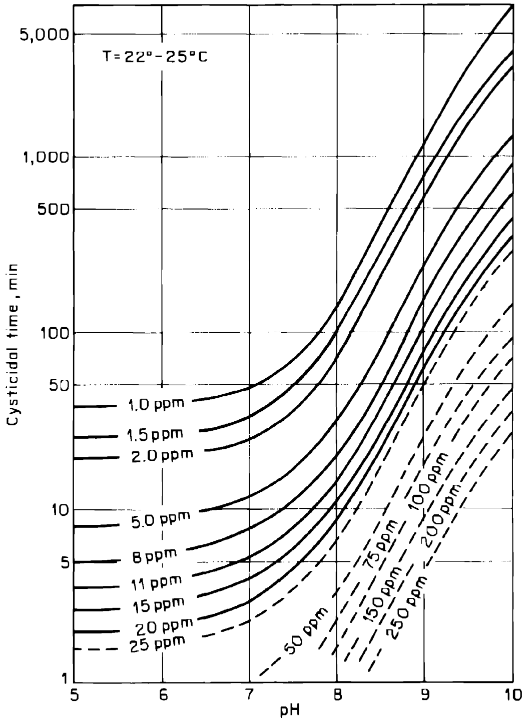

Fig. 9 Minimum contact time for free residual chlorine destruction of *E. histolytica*.[169]

lation; reduction of taste-, odor-, and color-producing materials by oxidation and retardation of decomposition (in settling units); and, importantly, the provision of a safety factor in disinfecting heavily contaminated waters while keeping chlorine residual in the distribution system at a minimum. When prechlorination is employed it is usually desirable to obtain a contact period which is as long as possible, preferably by applying chlorine to the raw water suction intake to provide contact during the entire purification process. The dosage, of course, depends on the objective. In some cases, free available chlorine residuals are indicated; in others, combined chlorine residuals may suffice. Care must be exercised to maintain the proper residual necessary to accomplish the desired objective, however, as some of the above benefits can be sacrificed when operating with reduced oxidation potentials of chloramines.

Postchlorination involves the application of chlorine to water subsequent to any other unit treatment process. The most important form of postchlorination is that following filtration for disinfection and to provide either free or combined residual chlorine in a part of or the entire potable-water distribution system.[183,184] The contact period provided to effect disinfection, as discussed elsewhere, is an important consideration; chlorine usually is added to the filter effluent or at the filter clear well. When postchlorination follows prechlorination and precedes filtration, greater filter efficiency is usually obtained. The second addition of chlorine raises the chlorine residual in the delivered water to a predetermined amount, thus reestablishing that portion of residual chlorine consumed in the purification process.

Rechlorination involves the application of chlorine to water, following previous chlorination treatment, at one or more points in the distribution system. The practice, which may involve free or combined residual chlorination, is especially common where the distribution system is long and complex and where the plant effluent residual is insufficient to control bacterial and algal regrowths, red-water troubles, etc. The chlorine may be applied at the end of a long main in the distribution system, at a point where a main supplies water to an outlying community, or at such places as reservoir, standpipe, or booster pumping station.

If a long contact period is available, combined available residual chlorine treatment may be employed as plain chlorination, prechlorination, postchlorination, or rechlorination. The points of application of ammonia and chlorine should be sufficiently far apart to permit thorough mixing of the ammonia with the water before chlorine is applied, but not so distant as to permit dissipation of ammonia by organic matter before chlorine is added. The earlier addition of chlorine may result in the formation of chlorphenols and other objectionable products. If a long contact period is not available, the general trend is to obtain free residuals through prechlorination and, later in the course of treatment, to convert the residual to a combined form that persists throughout the distribution system.

Dechlorination. When combined residual chlorination or free residual chlorination is employed, chlorine residuals of a certain type and intensity must be attained to accomplish a particular objective. In some instances, the residual might be of such magnitude as to render the water aesthetically or otherwise objectionable, and a portion of the residual will have to be removed. *Dechlorination is the partial or complete reduction of residual chlorine in water by any chemical or physical treatment.*

The origin of superchlorination-dechlorination applications has already been discussed. In the original applications, superchlorination was loosely understood to involve concentrations of chlorine greater than that required to provide the chlorine residual desired in the type of treatment now termed "combined residual chlorination." No recognition was given to the *type* of residual obtained, for differential residual tests had not yet been developed. In some instances and under some conditions, combined available chlorine residuals resulted from such treatment, while in other instances free available residuals resulted. The residuals were, however, sufficiently high to require dechlorination. Contemporary applications of the superchlorination-dechlorination concept are more suitably described as high free-residual chlorination followed by dechlorination. Such applications are especially suitable where available contact is very limited; they usually involve prechlorination in a water-treatment plant or plain chlorination in a pipeline, followed by dechlorination before the water reaches the distribution system.

Dechlorination by sulfur dioxide and its derivatives is feasible, rapid, and precise. These materials, often called "dechlors," function as reducing agents and may be applied ahead of filtration, in the clear well, or following plain chlorination. Sulfur dioxide was successfully employed by Howard[185] at Toronto in 1926, in connection with the first extensive North American plant application of superchlorination-dechlorination solely for eliminating tastes. Currently, it is the most widely used dechlor. Sodium bisulfite and sodium sulfite also are effective, but the former is ordinarily used in practice because it is cheaper and more stable. Sodium thiosulfate either in crystalline or solution form is commonly used to dechlorinate water samples intended for bacteriological analysis; its application on a plant basis appears to be limited to certain industrial water-treatment processes. It is also the standard titrating agent in the iodometric technique for determining residual chlorine [see Eq. (15)]. Some of the reactions and other matters pertaining to reducing materials are given in Table 5-5, which contains Eqs. 14-18.

Charcoal, lignite, and activated carbon had been used as dechlorination materials for certain industrial applications as early as 1911; it was not until much later that any attention was given to their possible utility in muni-

TABLE 5–5 Use of Sulfur Dioxide and Other Materials for Dechlorination

Dechlorinating agent	Parts required per part chlorine removed (theoretical)	Alkalinity consumed (as $CaCO_3$)	Equation
Sulfur dioxide, SO_2	0.90	2.8	$SO_2 + Cl_2 + 2\ H_2O = 2\ HCl + H_2SO_4$ (14)
Sodium bisulfite, $NaHSO_3$	1.46	1.38	$NaHSO_3 + Cl_2 + H_2O = NaHSO_4 + 2\ HCl$ (15)
Sodium sulfite, Na_2SO_3	1.77	1.38	$Na_2SO_3 + Cl_2 + H_2O = Na_2SO_4 + 2\ HCl$ (16)
Sodium thiosulfate, $Na_2S_2O_3$	0.7	. . . .	$2\ Na_2S_2O_3 + Cl_2 = Na_2S_4O_6 + 2\ NaCl$ (17)
Activated carbon, C	0.085	2.1	$C + 2\ Cl_2 + 2\ H_2O = 4\ HCl + CO_2$ (18)

ipal water treatment. Experimenting with a variety of carbons for control of tastes and odors associated with chlorphenol formation in 1928, Baylis[186] suggested possible superiority over sulfur dioxide for removing excess chlorine. Subsequently, others[187–191] reported further experiences that paved the way for extensive application of activated carbon for this purpose. Some observers[192] consider that the reaction represented by Eq. (18) is preceded by cumulative absorption of the chlorine. It has been demonstrated that powdered activated carbons are less efficient than granular carbons for dechlorination, presumably because contact with the former cannot generally be made long enough to produce this result.[185] Among factors influencing the selection of suitable carbons are particle size, adsorptive capacity, type and concentration of chlorine, flow rate, pH, and others.

Aeration of chlorinated water by submerged or spray aerators will lead to release of residual chlorine. In the case of free available residual, reduction is limited because calcium or sodium hypochlorite formed by the reaction of HOCl with natural alkalinity of the water is nonvolatile. Nitrogen trichloride, if formed, and free chlorine (Cl_2) can be readily volatilized by any type of aeration. At low pH levels (about 5) combined available residuals exist mostly as dichloramine, which is substantially reduced by aeration. At high pH levels (about 9), where monochloramine is predominant, very little loss of residual can be effected by aeration. Prolonged storage, especially in the presence of sunlight, also will result in the gradual disappearance of residual chlorine.

The successful experimental and plant application of controlled ammoniation for dechlorinating HOCl residuals at Brantford, Ontario, was recently reported by Williams,[150,193] although the possibility of ammonia dechlorination had been implied much earlier by others.[164,194] Laboratory experiences at Brantford involving a variety of inorganic ammonium compounds validated Palin's observations that 1.0 ppm HOCl can, in accord with theory, be effectively dechlorinated by 0.15 ppm NH_3. The method appears to be ineffectual for monochloramine reduction in particular and, to a lesser extent, dichloramine reduction in the presence of HOCl, whereas other materials such as sulfur dioxide are effective. Additionally, dechlorination by hydrogen peroxide and/or its derivatives[195] or by filtering through surface-active amine-condensation resins (e.g., a phenylene diamine diphenylene formaldehyde condensate) have been reported,[196] but the feasibility of such methods under variable operating conditions has not been established.

CONTROL OF WATER CHLORINATION

Chlorine Demand. As already indicated, the redox potential serves as a measure of the tendency chlorine has to react with other materials. Unfortunately, it is not a measure of the speed at which reactions will occur. In general, chlorine tends to react with fewer materials as pH is increased. Similarly the reactions that do occur generally are more rapid as the temperature is increased. Even under optimum pH and temperature conditions the oxidation of some materials may occur only slowly and sometimes requires an appreciable amount of time for completion.

Obviously the chemical characteristics of water sources differ tremendously as do, from time to time, though perhaps to a lesser degree, those of a single source. The amounts of chlorine necessary to accomplish a desired objective clearly reflect these differences. Thus, effective chlorination control necessitates adjustments in chlorine feed not only in relation to the variation in water flow, but also to compensate for variations in water quality. Principal among chlorine-reactive materials of concern in waterworks practice are inorganic reducing substances, ammonia, amino acids, proteins, and carbonaceous material. These materials consume the chlorine supplied, and the reactions may occur before disinfection is accomplished.

Materials in water that influence the chlorine demand complicate the use of chlorine for disinfection because sufficient chlorine must be applied not only to destroy organisms but to compensate for the chlorine consumed by these reactions. Reactions with inorganic reducing material generally are very rapid and stoichiometric; reactions with organic materials are generally slow, and their extent depends upon the excess of concentration of available chlorine present.

Where modification of the chemical characteristics of water is a desirable adjunct of chlorine disinfection, for instance to control tastes and odors of organic origin, the chlorination regimen is especially critical. For example, when a sufficient dose of chlorine is applied to yield a detectable residual, it will combine with organic materials, and the residual will be predominantly combined available chlorine. As more chlorine is applied to obtain a higher residual, the chlorine demand will be increased, and the remaining residual may include some free available chlorine. If sufficient chlorine is applied to yield a residual that is predominantly free available chlorine, the redox potential will be such that oxidation reactions prevail. Thus chlorine, instead of combining with organic materials that might cause undesirable tastes and odors, may completely oxidize them, destroying or changing them into less complex substances that do not cause disagreeable tastes and odors.

Chlorine demand is defined as the difference between the amount of chlorine applied to water and the amount of free, combined, or total available chlorine remaining at the end of a specified contact period. It expresses a definite equilibrium of chemical reactions of chlorine in water under known conditions. To achieve the desired equilibrium of chemical reactions it is not necessary to allow sufficient time and to provide an unreacted residual which may consist of free or combined available chlorine or both. For a particular water, the chlorine demand will vary with the amount of chlorine applied, the length of contact time, and the temperature. Determination of its magnitude must take all these factors into consideration. *Standard Methods*[197] defines two tests for determining chlorine demand, one for routine laboratory use and the other for field applications.

Residual Chlorine. The kind and amount of residual chlorine required for a particular application relate to the objectives of treatment and vary from time to time and place to place. Where disinfection is the objective, pH, temperature, chlorine demand, and organisms' vulnerability or resistivity to chlorine are primary considerations. With long contact periods, sometimes a low concentration of disinfection suffices, while short contact times require higher concentrations to accomplish equivalent kills. Moreover, the killing power of chlorine increases with rising temperature in addition to being markedly influenced by pH. Reference has already been made to the reduction of bactericidal power which occurs with increasing pH, in the case of free available chlorine, due to the degree of dissociation of HOCl and, in the case of uncombined available chlorine, due to the swing of equilibrium from dichloramine to monochloramine.

The control of chlorination processes is based on the attainment of a definite residual which, after the contact afforded, has been established by experimentation and experience to accomplish the purposes intended. Demonstration of bacterial (or other organism) destruction is the only *positive* way of establishing the efficacy of chlorine disinfection. Residual chlorine, manually or automatically determined, is the only *practical* way, however, for relating this with sufficient rapidity to plant operating control, and tests for the determination are universally employed for that purpose. Quality control by bacteriological testing coupled with statistical interpretations of results has become largely a matter of confirming treatment efficacy and providing a historical record to satisfy regulatory requirements.

Conventional methods for determining chlorine residuals depend on the oxidizing power of chlorine and are based on reactions with reducing agents. Basically three tests are currently employed: volumetric starch iodide (iodometric titration); modified colorimetric titration with orthotolidine; and amperometric titration.[197,198]

1. *Starch-Iodide Test.* The starch-iodide test[106] served as the only satisfactory basis of chlorination control until about 1913, when the orthotolidine test was developed.[112] It depends on the oxidizing power of free and combined chlorine residuals to convert iodide to free iodine:

$$HCl + HOCl + 2\ KI \rightarrow 2\ KCl + I_2 + H_2O \qquad (19)$$

In the presence of starch, free iodine produces a blue color indicative of the presence of residual chlorine; the depth of color is indicative of the chlorine content. Quantitative measurement of *total* residual chlorine (other oxidants react similarly) is achieved by acid titration of released iodine with a standard reducing agent solution, commonly sodium thiosulfate, using starch as the indicator:

$$I_2 + 2\ Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2\ NaI \qquad (20)$$

A familiar test to all waterworks analysts, it is, however, not always satisfactory as a means of treatment control, because when the chlorine concentration is less than 1 mg/l the titration endpoint is difficult to detect. Moreover, its utility is limited by the lack of specificity to chlorine as compared to other oxidants. Its principal applications are for calibration of stock chlorine solutions where total chlorine concentrations exceed about 10 mg/l, for preparation of chlorine water used in making temporary color standards, and for determining total residual chlorine concentration in excess of 0.04 mg/l.

2. *Basic Orthotolidine (OT) Test.* Orthotolidine is an aromatic compound that is oxidized in acid solution by chlorine, chloramines, and other oxidants to produce a yellow-colored complex the depth of which, at pH levels below 1.3, is proportional to the amount of chlorine and other oxidants present.[130,132] The test is especially suitable for routine determination of *total* chlorine residuals of 0.01 mg/l but not exceeding about 10 mg/l. The colorimetric OT test is sensitive, fairly rapid (about 5 min reaction time is required), and simple, but it is somewhat affected by natural color and turbidity, temperature variations, nitrites, ferric and especially manganic ions, and possibly by organic iron, lignocellulose, algae, and other materials. Because of these inherent limitations and difficulties in compensating for many of them, some investigators believe that the basic test is unsuitable for research applications and for continuous automatic recording of chlorine residuals. The test is widely used for routine meassurement of residual chlorine in plant control and in the field.

An orthotolidine flash test modification,[126,127] performed near 1 °C to minimize the effect of chloramines and their reaction with orthotolidine to produce a yellow color, can be used for the qualitative determination of *free* available chlorine in excess of 0.3 mg/l. Although oxidized manganese affects the test results, slow-acting interfering substances, nitrites, and oxidized iron do not have such a significant influence. The flash test has the disadvantage of requiring the reading of color (and matching color standards) within 5 sec. It is an exceedingly useful and simple control procedure where it is necessary to maintain a definite amount of free available chlorine.

With the development of current concepts of free and combined available residual chlorination, test methods have been designed to permit better differentiation and quantitative evaluation of residual chlorine forms. Two test methods are commonly employed for this purpose.

3. *Orthotolidine-Arsenite (OTA) Test.* The unique characteristics of sodium arsenite as a reducing agent led to the development of the OTA test for quantitative determination and differentiation of *free* and *combined* available chlorine forms. The test[133–135] is based in part on the fact that free chlorine residuals react instantaneously with orthotolidine, whereas combined residuals react slowly. *Total* chlorine is first determined by the OT method (as previously discussed), with reading made after 5 min. Another test is made on a fresh sample, adding sodium arsenite reducing agent immediately (within 5 sec) after the orthotolidine; this permits oxidation of orthotolidine by free chlorine but allows only a small part of combined chlorine to react before the addition of arsenite (which reduces the chloramines instantly, preventing further reaction with orthotolidine) and subsequent color development. The resulting color intensity of this sample thus is primarily a measure of free chlorine. If interferences are present, additional test modifications are indicated to correct the values of total and free chlorine; the addition of sodium arsenite before the orthotolidine is added neutralizes all chlorine compounds in the water, and any color formed is due to the reaction of interfering substances with the orthotolidine.[136]

Both the OT and OTA test methods can be rapidly completed by simple visual apparatus or by photometric techniques. Various residual chlorine test kits employing permanent glass or liquid OT color standards are available and widely used. Most units are designed to compensate for the effects of color and turbidity.

4. *Amperometric Titration Test.* The most accurate and complete test for determining total residual chlorine or for differentiating free and combined forms involves the use of an amperometric titrator with specific reagents and within specific pH ranges in sequential steps similar to those discussed above. The titrator is used to determine the endpoint of a titration which is accomplished through the addition of a reducing agent. Current flow is proportional to the oxidant concentration and decreases as the

oxidation-reduction reactions progress. When these reactions are complete, the current flow will remain quite constant (the endpoint of the titration) and will not be decreased by further addition of the reducing agent.

A standard solution of phenylarsenoxide (C_6H_5AsO), the reducing agent normally used in the titration, quantitatively reduces free chlorine (and, proportionately, current flow) at a pH of between 6.0 and 7.5 but does not react with combined chlorine in this pH range. Phenylarsenoxide quantitatively reduces combined chlorine in the presence of potassium iodide in the pH range of 3.5 to 4.5. Accurate determination of free chlorine cannot be made in the presence of nitrogen trichloride, chlorine dioxide, other halogens, copper, and silver, but other substances that interfere with the OT test (such as manganese, nitrite, and iron) do not affect the amperometric test. This test method is, of course, unsuitable for field use, and it involves a greater degree of skill and care than those methods described previously.

An adaptation of the amperometric technique currently having *Standard Methods* tentative status is available for differentiation of monochloramine and dichloramine. The differentiation depends on the fact that monochloramine reacts more readily with iodide than does dichloramine. Different iodide concentrations and pH values are used for separate determinations. The adaptation is subject to the usual interfering influences; in addition, nitrogen trichloride, if present, titrates partly as free chlorine and partly as dichloramine, and it cannot be determined in which fraction any organic chloramines that might be present will titrate.

5. *Other Tests.* Other test methods developed and refined by Palin[137,138] for differentiating available chlorine forms, also having *Standard Methods* tentative status, involve serial titration using orthotolidine as the indicator. At a pH of 6.3 to 6.5 and at 20°C, free chlorine, nitrogen trichloride, and chlorine dioxide form a blue color with orthololidine which can be titrated to decolorization by standard ferrous ammonium sulfate solution. By adding a trace of potassium iodide, monochloramine concentration can be similarly determined (in addition to some organic chloramines). Dichloramine concentration can be determined in a third step by adding sulfuric acid and more iodide, buffering with sodium carbonate to a pH of 6.5, and titrating again with the ferrous ammonium sulfate solution. Interferences due to chlorine dioxide, trichloramine, and manganese can be determined, but organic chloramines, as in the amperometric titration technique, titrate either as monochloramine or dichloramine. The complexity, time, and skill required in the performance of the complete differentiation currently limits application of the technique to research and specialized plant control problems.

In Palin's *N*, *N*-diethyl-*p*-phenylene diamine (DPD) monohydrochloride test method,[139] reagents in granular or compressed-tablet form can be used.

With free chlorine the indicator produces a red color. Like the Palin method using orthotolidine as the indicator, free chlorine, monochloramine, and dichloramine can be determined, and interferences can be suppressed using appropriate chelating agents.

The determination of chlorine dioxide is quite simple when this material is in solution by itself, and any of the techniques for chlorine may be adapted for the purpose. When present with hypochlorous acid, its determination is difficult. At concentrations in excess of 0.2 mg/l it can be determined specifically with tryosine, but this colorimetric procedure is not considered sufficiently sensitive for most water-treatment plant needs. The determination of chlorine dioxide in the presence of chlorine can be accomplished with the usual techniques for measuring chlorine after the latter has been preferentially reduced by oxalic or malonic acid.[140,141,198,199]

Automatic Residual Indicators and Recorders. Where variations in chlorine demand are erratic and fluctuate between wide limits, a continuous indication and record of residual chlorine is especially desirable. Equipment for this purpose is an essential part of automatic-chlorination instrumentation and can be installed in any convenient location at or remote from the sampling cells.

Where residual chlorine recording facilities are provided, more effective and economical chlorination practices are assured. Residual and recording systems are especially useful in detecting and compensating for sudden or natural changes in chlorine dosages and furnish a permanent record of the efficiency of chlorine treatment. Remote location of recorders facilitates efficient and prompt adjustments of chlorine feed from central operating stations and minimizes the necessity of continuous, on-the-spot surveillance of treatment facilities.

A variety of commercial units are available. Some units operate on the production of an electric current between two suitable electrodes and translate this current (proportional to the chlorine concentration) to an indicator and recorder. Depending on the pH value of the sample and the test reagents employed, free or total available chlorine residuals can be recorded. Other units involve photoelectric measurement of color intensities produced by orthotolidine or starch-iodide and automatically compensate for the effects of sample color or turbidity. Most units can be equipped to control chlorine feed to maintain a desired residual.

Chlorine flow-rate recorders also offer many advantages. For example, they provide evidence and a permanent record of operation at or away from the chlorinator site and provide a constant check on chlorine consumed. These records are useful in determining correct dosages, seasonal and other variations in chlorine demand, and in evaluating other valuable operating information. A variety of commercial units are available that can be tied in with optional alarm equipment.

Chlorine Feeder Instrumentation. The principles and operation of chlorine feed equipment are discussed in Chap. 17, "Chemicals and Chemical Handling." The most elementary form of chlorination control involves manual adjustment of the chlorine dosage as may be necessary. The earliest and most simplified form of automatic control provided for automatic maintenance of a fixed dosage in proportion to variations in water flow. Later, additional forms of automation emerged which greatly enhanced the efficiency of chlorine treatment and simplified control by operating personnel. Among some schemes employed are the following:

Semiautomatic control—The chlorine feeder is automatically actuated by pumps or timers to deliver a fixed, manually preset chlorine dosage. In multiple-pump installations, a step-control regimen can be provided, and chlorine feed is automatically synchronized to provide proper dosage for one or a combination of pumps in operation. "Start-stop" operation is a form of semiautomatic control.

Program control—Chlorine dosage is automatically varied in accord with a preestablished time schedule. This type of control is utilized more frequently in waste chlorination than for water treatment.

Automatic proportional control—The chlorine feeder automatically and continuously adjusts chlorine feed rate in accord with changes of flow to provide a constant, preestablished dosage at all flows. The desired dosage is manually preset by the operator, and by means of various flow-measuring devices, the chlorine feed rate is automatically controlled.

Most proprietary chlorine feeders can readily be adapted to program, semiautomatic, or automatic proportioning control by responding to a vacuum, pneumatic, or electrical transmission signal of primary metering elements. The transmitted signal regulates the chlorine feed in direct proportion to the main volume of flow. Where dosage is more advantageously controlled at a point remote from the feeder, most equipment can be so set up as to provide for immediate adjustment of the chlorine flow as and when needed. At such installations, an indicating chlorine-flow transmitter at the feeder location and a flow recorder at the remote station are often provided.

These schemes, by themselves, respond only to changes in flow (quantity) and do not automatically compensate for variations in chlorine demand (quality). Unfortunately, maintenance of a fixed chlorine dosage often does not provide that a chlorine residual necessary to accomplish the treatment objective will be maintained. Moreover, when chlorine requirements fluctuate due to water quality variations, it is difficult to adjust the dosage to prevent application of too much or too little chlorine. One of the early instrumentation schemes devised in an attempt to overcome this shortcoming is based on oxidation-reduction potential (ORP) process control.[200,201] ORP control is quantitative only, for it simply indicates the presence or absence of free or combined available chlorine. Briefly, it involves measurement and maintenance of an oxidation potential level (a function of the type of chlorine present) which ensures the desired results. Application of this scheme has not gained wide acceptance.

Recently other approaches to fully automatic chlorine-feeder control have been devised which account for changes in both flow and chlorine demand. In some units, the amount of chlorine required to produce the desired residual is measured and recorded as chlorine demand. Other units measure and record the actual chlorine residual and control to the desired residual. In these schemes, signals from the demand or residual recorders together with a signal from a flow-measuring device can be fed to the chlorine feeder which automatically responds in accordance with both quality and quantity variations.

Statutory Control. Control of water quality in the United States and, accordingly, methods of treatment are under the jurisdiction of the various states and their political subdivisions. Probably without exception, all 50 states have legislative authority to exercise control over the sanitary quality of public water supplies and the design and operation of new facilities.[202] At least 30 states publish minimum standards of design, construction, operation, and maintenance of public water facilities. About one-third of all the states rely almost exclusively on the *Ten-state Standards*,[203] a guide prepared in 1950 by a committee of the Great Lakes–Upper Mississippi River Board of State Sanitary Engineers. The United States government has no direct control over the quality of public drinking water except for the water used on interstate carriers. The Public Health Service, however, has published recommendations on water-treatment practice[204] that are intended as a *guide* to treatment-plant operators and several state and other review authorities.

Very few states have established rigid limiting bacteriological criteria or acceptable raw water sources. In general, those water sources that can be rendered bacteriologically and chemically safe by reasonable treatment are considered satisfactory. A raw water MPN coliform concentration of 20,000 appears to be accepted as the maximum safe limit for prechlorination, rapid-sand filtration (or equivalent), and continuous postchlorination. Walton's data[205,206] indicate that coagulation, sedimentation, and filtration as currently practiced are inadequate for treating waters with an MPN coliform density exceeding approximately 50, and that plant superintendents must provide supplementary treatment by continuous and adequate chlorination at any plant which treats waters having substantial coliform densities. Not all states require disinfection of all public surface and groundwater supplies, but a majority of states require or recommend terminal disinfection (chlorination) of all surface water sources as a minimum safeguarding treatment, regardless of raw water quality. Chlorination is not to be a *substitute* for more general treatment. Waters high in color or noticeable turbidity or carrying industrial wastes in solution require other forms of treatment which often are enhanced if chlorination is an integral part of the total purification process.

Similarly, only a few states have fixed policies with regard to points of chlorine application, chlorine contact periods, plant or distribution system residuals, or frequency of testing. Almost invariably these are related to local considerations and treatment objectives. As a minumum, good practice implies provision for, and continuous application of, chlorine to the plant effluent. Additionally, provisions for chlorine application to the raw water at various points in the treatment process and in the distribution system are becoming increasingly popular.

Maximum chlorine contact periods consistent with treatment objectives and operational characteristics are desirable. The *Ten-state Standards* specify a minimum contact of 30 min where free residual chlorination is the only treatment. USPHS recommendations provide for minimum total contact periods of 20 min in places where free residual chlorination is practiced and, preferably, 3 hr in places where combined residual chlorination is practiced.

The usual requirement is that chlorine disinfection facilities be operated and maintained in such a manner that a fixed, minimum residual is obtained which, on the basis of local experience, can be demonstrated to yield a water of satisfactory bacteriologic quality. Standards of quality usually referred to by state authorities are those of the USPHS.[207] In general, safe and desirable minimums of free and combined residual chlorine at distant points in a water distribution system are about 0.05 to 0.1 ppm and 1.0 to 2.0 ppm, respectively, depending on pH, temperature, and other characteristics of the water.[204]

Minimum chlorine-feed equipment capacities are rarely defined by state statute. The *Ten-state Standards* provide that the capacity of solution-feed equipment be such that a minimum chlorine residual of 2 ppm be attainable after 30 min contact, even when maximum flow rates coincide with anticipated maximum chlorine demand; and, further, that automatic proportioning feeders be used where flow rate is not reasonably constant or is not manually controlled. USPHS recommendations provide that chlorine-feed equipment be of such capacity as to exceed the higher expected chlorine dosage (without the use of standby equipment); and, further, that automatic proportioning feeders be used at all larger plants where the rate of flow varies more than 50 per cent more or less than average flow and where water quality is subject to change without warning. Both authorities stress the necessity of providing adequate standby equipment to ensure uninterrupted operation and of maintaining spare parts and tools for emergency replacements or repairs.

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6

Taste and Odor Control

By A. A. ROSEN and R. L. BOOTH

IMPORTANCE OF ACCEPTABILITY

The constant safety of potable water supplies is rightfully assumed and taken for granted by today's public. In addition, consumers are increasingly demanding that water purveyors provide a product that is agreeable in its taste and odor qualities. This importance of customer satisfaction plays a vital role in the economics of water treatment. Thus, in many municipalities, greater amounts of money are required to improve the aesthetic quality of the water to make it acceptable than are needed to guarantee its safety.

The relative health significance of striving for maximum water quality in terms of its taste, odor, and appearance should be obvious. The repeated presence of objectionable tastes, odors, and colors in a water supply may cause the public to turn to other water resources—resources, that for the most part, are not reliably safe from a health viewpoint. It should also be recognized that incomplete removal of taste- and odor-bearing substances suggests to the layman the possibility of potentially toxic chemicals being present in the unsatisfactorily treated water.

PHYSIOLOGICAL BASIS OF TASTE AND ODOR

The unassisted sense of taste is able to detect the sourness of acid, the sweetness of sugar, the bitterness of quinine, and the salt taste of sodium chloride.[1] In comparing the sensitivity of taste to odor, one can think of taste as being used in determining the presence of large amounts of substance, and smell for only the most minute quantities. As any water plant operator knows, however, the most frequent consumer complaint concerns the "taste" of the water. This, of course, is due to the sensation realized from the natural combined action of the chemical senses of taste and smell.

Many theories have been advanced concerning the mechanism of odor sensation, some attracting more interest than others. No one theory, however, has become commonly accepted, for none of the proposed theories have been able to satisfactorily explain experimental data and observations.[2,3] Investigations are still being conducted in this area and advances are being reported.[4] Pending the evolvement of a satisfactory theory, it should be noted that no theory of odor stimuli is required for the development of useful experimental data in both research laboratories and water-treatment plants.

PSYCHOLOGICAL BASIS OF TASTE AND ODOR SENSATIONS

There have been many attempts to systematize odor sensation, but in all cases there were obvious limitations to the method evolved. Some examples of the more publicized methods are Zwaardemaker's listing of nine basic types of odors, Henning's sixfold arrangement in the form of a hollow triangular smell prism, and the Crocker-Henderson system, which postulates four fundamental odors: fragrant, acid, burnt, and caprylic (goaty). These and other attempts to classify odor all have met with limited success because of the highly complex nature of odor sensation. This complexity is also apparent when efforts are made to characterize odor sensations in evaluating water quality. Thus, it is recognized that any tabulation of qualitative descriptive terms of odors has limited value and should be used only as a guideline.[5]

Another characteristic commonly used in attempting to fully describe an odorous substance is intensity, i.e., degree of perception. Generally speaking, an intensity rating scale is short and simple, ranging from no perception to strong in its descriptive terms. Once again, because of variations in individual backgrounds and experiences, observations will vary from person to person. The relationship between odor intensity and concentration of the odorous substance is not completely understood. Perhaps the most frequently mentioned "law" used in trying to quantitate this relationship is that of Weber-Fechner

$$S = K \log R$$

where S = sensation
R = stimulus

At its best, this simply states that apparent intensity is related to concentration in a complex manner. The relationship does not have universal applicability and is apparently of limited value.

Two closely related phenomena in relation to taste and odor sensation are fatigue and adaptation. Fatigue concerns a transitory deterioration in sensitivity induced by continuous stimulation. Quite often a given odor fatigues the sense of smell to the point where even increased concentrations cannot be detected. Individuals show variability in the rate of fatigue, and some odorous substances have more pronounced effects than others, so adequate rest is required between observations. Adaptation, on the other hand, involves an adjustment of one's odor sensitivity in response to certain environmental conditions. As a matter of fact, it is felt that we are partially odor-adapted most of the time.[2] The rate, type, and degree of adaptation varies with the type of odor stimulus involved; however, the stronger the stimulus the more rapid adaptation occurs.

The association of an odor stimulus with a specific chemical or frequently encountered type of odor is commonly used in characterizing odor. Certainly, one's background and experience play a major role in such descriptions. Environmental factors are also important in determining the hedonics of a given odor, i.e., pleasantness or unpleasantness of odor. Although hedonic scales[6] have been devised to measure an individual's response to a given taste and/or odor, it should be recognized that such a measurement does not necessarily predict its hedonic value when present in such a complex system as a water supply.

ODOR MEASUREMENTS

One of the more common techniques used to measure threshold odor in water is the Threshold Odor test. In this procedure, described in detail in *Standard Methods*,[5] a series of eight to ten coded odor flasks (200-ml sample in a 500-ml glass-stoppered flask) is presented to the observer. The observer is told that some of the flasks contain odor samples, some are odor-free blanks, and that the sample series is arranged in order of increasing concentration. The observer is also given a known odor-free blank for reference during the test. He compares each flask in the ascending test series with the known blank, noting whether an odor is detected in the sample flask. Ideally, there will be a minimum concentration in the test series that the observer calls odorous. The rest of the odor-bearing samples in the series will be detected and the intervening blanks will be judged inodorous. This minimum concentration is defined as the observer's threshold concentration for the sample under investigation and is simply the number of times the odor-bearing water is diluted with odor-free water.

A second technique for measuring odor intensity involves the use of rating scales. In these procedures the observer rates a series of samples in terms of his perceived intensity of some specified characteristic. One of the more common applications of such a method is the determination of previously described hedonic values[6] in which the observer is instructed to determine how much he "likes" or "dislikes" each sample and to mark the provided rating scale accordingly. Rating scales have also been used to report intensity of odor in water.[7] These are of questionable value since experienced observers tend to magnify small differences in intensity and, thus, record greater magnitudes of deterioration in odor quality than are actually present.

Individuals vary in their reactions to certain types of odors. Thus, an odor stimulus that is agreeable to one may be disagreeable to another. This difference in degree of acceptance of odor quality, the knowledge that some odors change with dilution, and that odors may undergo qualitative changes by continuous exposure are all further complicated when attempts are made to predict the odor intensity of mixtures. This is, of course, the exact situation existing in water supplies: namely, the presence in trace amounts of countless taste- and odor-bearing substances reacting in some combination to result in an observed "taste" in the water. The ultimate effects of odor interaction are independence, subtraction, addition, and synergism (enhancement).[8] Laboratory studies on known organic compounds[8, 9] and organic compounds recovered from water[10] indicate that odor addition is characteristic of mixtures, and that there is strong evidence of odor synergism.

CAUSES OF TASTE AND ODOR IN WATER

As discussed above, objectionable tastes and odors in water are normally due to combined circumstances. The materials that contribute to these observed tastes and odors come from many sources. Although some inorganic compounds, such as metal ions in concentrations of ppm, impart taste to water, the main sources of odor-bearing substances are organic materials. These materials, under certain conditions, can cause persistent difficulties when present in only trace amounts of a few parts per billion. They are also quite numerous and vary in complexity of structure, so that their recovery from water and ultimate identification is difficult.

Organic chemicals and specific compounds that are taste- and odor-bearing substances have been recovered from river water by use of the carbon adsorption method sampling technique[11] and subsequent identification by infrared spectrophotometry. Tables 6-1 and 6-2 are examples of the varied types of organic substances present in surface water and show, in many cases, the trace amounts required to cause taste and odor.

TABLE 6-1 Concentration of Some Chemicals Causing Taste and Odor[12]

Substance	Concentration detectable, ppb
Formaldehyde	50,000
Picolines	500–1,000
Phenolics	250–4,000
Xylenes	300–1,000
Refinery hydrocarbons	25–50
Petrochemical waste	15–100
Phenylether	13
Chlorinated phenolics	1–100

TABLE 6-2 Threshold Odor Concentration (TOC) of Some Individual Compounds[10]

Compound	TOC, ppb
Naphthalene	6.8
Tetralin	18
2-Methyl-5-ethylpyridine	19
Styrene	37
Acetophenone	65
Ethylbenzene	140
Bis(2-chloroisopropyl)ether	200
2-Ethylhexanol	270
Bis(2-chloroethyl)ether	360
Di-isobutyl carbinol	1,300
Phenylmethyl carbinol	1,450

Using comparable methods, Holluta[13] has studied taste and odor problems due to mineral oil products and various constituents of petroleum. It is now well established that pure alkylbenzene sulfonate (ABS) is nonodorous.[14,15] The reported odor incidents associated with detergent pollution are evidently due to perfumed additives or contamination by chemical raw materials.

Odor characteristics of organic pollutants recovered from waste outfalls of various industries have also been determined.[16] Of those studies, it was found that the chemical and refinery samples had the greatest potential for odor. Domestic wastes were sampled too, and were found to fall between the most and the least odorous of the waste samples. These sewage wastes, depending upon the degree of treatment and at what stage they are released into a stream, are a major source of odorous substances.

Biological materials are one of the most common causes of taste and odor in water. Thus, in a survey[17] of water plants across the country, algae were listed as the most frequent substances causing taste and odor problems in water supplies. It was further reported that diatomaceae were the most responsible, with *Asterionella* and *Synedra* being the principal offenders. A comprehensive report[18] enumerating all the different types of algae of importance in connection with water supplies and taste and odor problems has been prepared. Research on the actual sources of algal odors has shown that the responsible compounds are a result of the metabolic activities of algae and that, for the most part, the odoriferous material is retained within the cells of the algae until their death or disintegration.[19]

Actinomycetes are another biological source of taste and odor in water, imparting a characteristic earthy, musty-type odor. Silvey[20] has studied this particular area of research extensively over an extended period of time, and field studies[21] have been made in which actinomycetes have been implicated as the cause of persistent and troublesome taste and odor problems. More recent research investigations[22] on actinomycetes and their relationship to odor in water have been made. Concentrates of the odoriferous material, metabolites of an isolated culture, *Streptomyces griseoluteus*, showed high odor intensities with threshold numbers in the billions.

Free-living nematodes and amoebae are a third general biological source found in municipal water supplies. Cultures of nematodes, taken from various rivers throughout the country, were found to produce an oily, gummy substance that had a distinct earthy or musty odor.[23]

The distinct possibility of taste and odor problems developing in the distribution system and, thus, causing unpalatable drinking water cannot be ignored. Such incidents are normally found to be due to the delayed reaction of chlorine, being routinely used as a disinfectant, with organic compounds present in the finished water. For example, it has been shown that the chlorination of phenol, by itself relatively tasteless and odorless, results in the formation of intermediate chlorophenols that are highly odorous.[24] The duration of these intermediate compounds is affected by such environmental factors as pH, temperature, presence of ammonia, and concentrations of reacting species. If the water is consumed during this period, i.e., before complete chlorination occurs, typical chlorophenolic tastes and odors will be apparent and, consequently, result in unacceptable water.

CORRELATION OF ODOR WITH ANALYTICAL DATA

A number of studies have been made to relate observed taste and odor conditions to the organic chemical content of the water. The previously mentioned carbon adsorption method[11] has been used as the sampling device, for the most part, since large volumes of water are required to yield adequate sample extracts of the trace organic contaminants suspected of being the odor source. Larger quantities of extracts are obtained by using a large-scale carbon filter arrangement.[25] Essentially, the method consists of removing the organic substances from water by adsorption on activated carbon. After being dried, the carbon is serially extracted with chloroform and ethyl alcohol to remove the organic material from the carbon. The chloroform extract, which normally contains the odoriferous substances, is separated into fractions based on solubility differences. Studies[26–29] on various water systems throughout the world have shown that the neutral fraction so obtained by this procedure contains the most significant taste- and odor-bearing substances of the sampled water. Odor tests made on these isolated fractions indicate that only a few parts per billion of these materials are needed to produce a detectable odor. Using comparable procedures, it has also been shown that there is a direct relationship between the amounts of organic material recovered and the odor intensity observed in the sampled water.[30,31] Thus, large amounts of chloroform extractables are recovered from waters where high odors occur.

TREATMENT OF ODOR

There have been a number of excellent review articles written on the causes and, especially, on the treatment of odor.[32–37] A chapter on taste and odor control has also been recently published.[38] In the following discussions on the treatment of odor, two general approaches are considered: destruction of odor and removal of odor.

Destruction of Odor

Frequently used techniques for the destruction of odor are based upon the oxidation of odorous substances to innocuous forms. Chlorination, used primarily for disinfection purposes, is probably the most popular of the oxidation methods. Reviews[39,40] tracing the developments in the use of chlorine and its compounds to control taste and odor have been compiled. In addition to being a strong oxidizing agent, free chlorine also controls the growth of odor-causing algae and microorganisms, thus removing additional taste- and odor-bearing substances from the water system. Four major groups describe chlorination practices: combined residual chlorination (chlorine-ammonia treatment); free-residual chlorination (breakpoint process); superchlorination and dechlorination; and chlorine–chlorine dioxide treatment.[41] Regardless of the process used, sufficient amounts of chlorine must be available to ensure complete oxidation; otherwise, intermediate chlorinated compounds may intensify any existing tastes and odors. Such variables as pH, temperature, quantity, and type of organic matter in the water influent have a marked effect on the efficiency of removal of odorous materials and the detention times required to ensure palatable water.

Chlorine dioxide, an unstable, unpleasant smelling, irritating gas at ordinary temperatures and pressures, is generated as needed at the water-treatment plant by the addition of sodium chlorite solution to chlorine water. Normal practice is to use an excess of chlorine, since it is cheaper, and the surplus acts as a disinfectant. Chlorine dioxide, more chemically active than chlorine, oxidizes odorous substances at a higher rate and has been used successfully in destroying chlorophenols and other odorous substances.[42,43]

Another oxidant used to control taste and odor is ozone. It, too, must be generated as needed. Various ozone-generating apparatus are commercially available. Essentially, the system involves passing extremely dry, clean air through a special form of high-voltage electric discharge. The mixture of air leaving the generator contains about 1% ozone (O_3), which is passed through the water to be treated. Typical dosages are 8 to 50 lb of ozone per million gal of water.[44] It is interesting to note that in France the primary purpose of ozonation is disinfection, and the removal of tastes, odors, and color are secondary effects.[45] Ozone treatment is generally most effective in waters having high threshold odors, being of less value when odors are moderate to low.[46]

Potassium permanganate, steadily gaining in water-treatment use since about 1960, acts effectively as an oxidizing agent in destroying tastes and odors.[47–49] It also readily oxidizes soluble iron and manganese to insoluble oxides that are subsequently removed by coagulation, sedimentation, and filtration.[50] Some method of filtration is always necessary when potassium permanganate treatment is used in order to remove the insoluble manganese oxide hydrates formed during the process. Although there are various points in the treatment system where permanganate may be added, either as a solid or in solution, it is normally applied in pretreatment at the rapid mix. It may be added before, during, or after chlorination; however, if organic substances capable of forming odorous chloro derivatives are suspected of being present, chlorine should not be used before the permanganate is consumed. It is also advisable to complete this treatment before adding ferrous sulfate or activated carbon. Normal dosage, varying with water quality conditions, ranges between 1 and 5 ppm. Effective visual control is possible because of the characteristic pink color of potassium permanganate in solution.[51]

In addition to oxidants, there are other materials that are used to prevent taste and odor. Thus, copper sulfate has proven quite effective as an algicide in raw water supplies, eliminating odorous substances due to algae. It is also used alone or in combination with ammonia and chlorine fed into finished water to control any aftergrowths of algae.[52] Biological methods have been used to control actinomycetic taste and odors.[37] A blue-green algae virus has been isolated and shown to infect and destroy freshwater algae,[53] thus affording still another method for controlling odorous substances due to algae.

Removal of Odor

Many of the common water-treatment processes aid in the removal of odorous substances from water. Among them are aeration, coagulation and flocculation, sedimentation, and filtration. Depending on the physical and chemical conditions of the water at the time of treatment, each process has varying degrees of efficiency.

Aeration, principally used to oxidize soluble iron and manganese and to liberate hydrogen sulfide and carbon dioxide, successfully removes highly volatile organic substances from water. While seldom, if ever, used as the sole source of odor removal, it does decrease the amounts of materials required to remove any remaining odors. There are basically two types of aerators: those that expose water to the atmosphere and those that form small bubbles of air that rise in the water. Examples of the former are spray and waterfall aerators and of the latter, diffused-air aerators.

Coagulation and flocculation are two important steps in the overall operation of a water-treatment plant. Coagulation is the addition of chemical agents to facilitate the settling out of suspended solids and colloidal matter. This requires rapid mixing at the point of application in order to ensure uniform distribution of the coagulating agent throughout the system. Subsequent mixing of the water by gentle agitation for a period of time in which the small particles of matter grow, coalesce, and agglomerate into well-defined flocs is termed "flocculation." These flocs, which now settle quite readily, may remove odorous substances from the water by adsorption of soluble materials and/or trapping of insoluble compounds. The final deposition of this settleable matter occurs in the sedimentation basins and yields a water that is normally lower in odor potential.

Filtration, the final step in the removal of particulate matter from water, involves the separation of suspended matter from water by passage through sand. There are two general types of sand filters—slow and rapid. The latter are of two types, the widely used free-surface type and pressure filters. Here again, odor removal is by adsorption and/or trapping of refractory materials by the sand filter beds. As with the previous plant treatment procedures discussed, palatable water is seldom produced by this process without some form of additional chemical treatment. This is especially true when there is a high concentration of tastes and odors in the water influent.

Another method for odor removal that has not been thoroughly explored involves removal by extraction. Patents[54] have been issued on such procedures; however, because of economic considerations such techniques are not practical for water treatment and, except in special cases, would have limited value. Essentially, the technique consists of concentrating the organic materials by emulsification and recovering them by subsequent extraction with an appropriate solvent system.

Adsorption of odorous substances from water is a common technique for the treatment of odor removal. Various adsorbents have been investigated as potential treatment agents;[55] however, practical experience has shown activated carbon to be the most capable of consistently producing a palatable water at comparatively low cost. Accordingly, activated carbon treatment is discussed separately.

Activated Carbon. Years of experience in successfully treating odorous water with activated carbon have resulted in its universal acceptance as the best all-purpose treatment procedure for taste and odor control. As evidenced by Table 6-3, there are many sources for the raw material used in the manufacture of this product.

TABLE 6–3 Abridged List of Source Materials for Activated Carbon[56]

Bituminous coal
Bones
Coconut shells
Lignite
Peat
Pecan shells
Petroleum base residues
Pulp mill black ash
Wood

Essentially, activation processes consist of the source materials being carbonized under controlled conditions and the resulting carbon being treated with an oxidizing gas, such as steam or air, at elevated temperatures.[56] The adsorptive properties of the finished product are, of course, determined by both the source material used and the activation process employed. The presently accepted method for evaluating the adsorption capacity of a given carbon is by determining its "phenol value." That is, "the amount of carbon, expressed in parts per million, required to reduce [a] standard phenol concentration of 100 ppb to 10 ppb phenol."[57] Most commercial carbons have a phenol value in the range of 15 to 30.

There are basically two types of activated carbon used in water treatment: powdered and granular. The powdered carbons are predominantly used in routine water-treatment practices, being applied as batch processes. The granular carbons, used in the form of carbon adsorption beds, have not been used extensively in water treatment because of economic considerations.

Powdered Carbon. This carbon is a finely ground, insoluble black powder that can be applied to water either through dry feed machines or as a carbon slurry. Feeding machines specifically designed for handling activated carbon are now commonly available. As enumerated by Sigworth,[58] the following factors should be considered in purchasing such equipment:

> (1) The machine should have ample capacity to handle any situations which may develop in the foreseeable future. (2) The machine should be so designed that carbon will feed continuously to the proportioning mechanism. (3) The proportioning device should provide a fairly constant delivery of the volume of carbon required. (4) The solution pot should be amply designed to provide for complete wetting of the carbon particles at the maximum rate of feed. (5) Proper facilities must be provided to deliver the carbon slurry to the point of application even at high rates of speed. (6) Since activated carbon is an extremely fine black powder, the feeding machine should be equipped with a suitable dust collector.

Slurry methods are sometimes used, especially in metropolitan water-treatment plants where large quantities of activated carbon are required. In such cases the carbon is normally supplied in bulk hopper cars, transferred to underground storage tanks, wetted with water, and stored as a slurry until needed.

Activated carbon can be applied to the water at any treatment stage before filtration. The optimum point of application is dependent on a number of interrelated factors that must be properly evaluated in terms of overall treatment. Although the proper point of application is, by necessity, a matter of individual study, certain aspects of the selection procedure can be discussed. Thus, sufficient contact times between carbon and the taste and odor compounds are necessary to ensure maximum adsorption by the carbon. Periods of contact ranging from 10 to 15 min or more have been recommended.[59] Adequate dispersion of the carbon is also necessary, so that very few plants use their settling basins as application points. The effect of other treatment procedures must be considered. For example, the addition of softening chemicals, by raising the pH of the water, makes it more difficult for carbon to adsorb odorous organic compounds and, in general, more carbon is required to produce a palatable water when chlorine is applied before carbon than when carbon is applied before chlorine.[59] The amounts of carbon required to successfully combat odorous materials will, at times, determine the point of application. Addition at the filter influent should not normally exceed 30 lb per million gal (3.6 ppm), except for short durations and only with sand filters that are in excellent condition.[58] For situations where odor conditions are extreme and larger doses of carbon are required, application is normally made at the mixing basin. This has the added advantage that the carbon particles which subsequently settle out with the floc stabilize the sludge in the settling basin.[60]

The laboratory tests used in determining the optimum dosage of activated carbon required for producing palatable water were thoroughly presented in the preceding edition of "Water Quality and Treatment."[61] Except for updating references and minor revisions, this subject matter is reproduced in the following discussion.

> Laboratory tests for determining optimum dosage are usually conducted on samples of about five gallons of water collected from a point where carbon treatment would be practical or, if it is already being applied, from a point ahead of the application. Fresh samples daily are always preferable, and become essential when the character or intensity of the odor changes on standing. *All equipment used in the test, including the sample container, should be absolutely clean and should be rinsed with odor-free water before use.*
>
> In making dosage tests, one-liter samples of the water to be tested should be placed in containers of such size and shape that they can be used in a laboratory stirring machine. No more than five samples should be tested at one time, including a sample of untreated water to act as a control, or blank. Containers should be placed in the stirring machine and the stirring mechanism started at a rate of about 100 rpm. Four of the five samples of water should then be treated with incremental dosages of carbon. This is best accomplished by using a stock carbon slurry prepared by mixing exactly 1.0 gram of carbon in 1,000 ml. of odor-free water, making the addition of 1 ml. of the stock suspension to 1 liter of water equivalent to a dosage of 1.0 ppm. If extremely high carbon dosages are necessary, this stock suspension would, of course, result in too great dilution of the sample, so that a more concentrated suspension would be advisable. The suspension used should be thoroughly shaken each time a sample is to be withdrawn and should be freshly prepared each day.
>
> Carbon dosages selected for test will depend upon the concentration of odor in the water and the ease with which it is removed by carbon. Table 6-4 may be used as a basis for starting the work. Then, after the proper carbon dosages have been applied, the samples should be stirred for a period of time equivalent to the detention period in the plant. Record should be made of the exact time selected and that period should be maintained uniformly in all succeeding tests.

TABLE 6-4 Determination of Proper Carbon Dosage for Different Odor Concentrations

Threshold odor of untreated sample		Carbon dosage, ppm			
	Container 1	Container 2	Container 3	Container 4	Container 5
10-20	None	2	4	8	16
20-40	None	4	8	16	32
40-80	None	8	16	32	64
Over 80	None	10	20	40	80

Following the stirring period, samples should be removed from the stirring machine and filtered. Filtering is best accomplished by the use of narrow-mouthed Erlenmeyer flasks in which are placed Buchner-type funnels, containing about a half-inch depth of very fine glass wool. While samples are being stirred, the glass wool should be washed at least two times with odor-free water to eliminate any possible contamination. Samples should then be run through the filters, the first 200 ml. of effluent being discarded and the remainder of the samples retained for threshold odor tests. Before conducting odor tests, the samples should be coded by some disinterested person to assure freedom from even unintentional bias on the part of the operator. The "Threshold Odor Test" method, as described in *Standard Methods*[5] should be used.

After odors have been determined, results should be plotted, preferably on log-log paper in accordance with the Freundlich equation.[57] Arithmetic plots, however, are quite satisfactory and, in the interest of simplicity, are used here for illustration.

Assuming for Water A that carbon dosages of 2, 4, 8 and 16 ppm. gave threshold odor numbers of 9, 6, 3, and 2 respectively on water having a beginning odor concentration of 20, the results would plot as shown in Fig. 1. If an odor concentration of 5 is normally considered a satisfactory water, it will be seen that a carbon dosage of about 5 ppm. is indicated. Assuming, then, that the odor in Water B under examination had an odor concentration of 200, and carbon dosages of 10, 20, 40, and 80 ppm. gave threshold odor numbers of 70, 40, 20 and 8 respectively, the results would plot as shown in Fig. 2. If an odor concentration of 5 is necessary it will be noted that a dosage of 80 ppm. in the laboratory is insufficient. It is not good practice to extrapolate beyond actual results on arithmetic plots. Results should therefore be plotted on log-log paper, or tests should be run using higher dosages, and if new tests are run a complete series should be used. Results obtained at one time are not necessarily comparable with those obtained later, due to varying sensitivity of the operator.

If a complete study is to be made, jar tests should be run using various carbon dosages in combination with other chemical treatments. Only one variable, however, should be altered in each series of tests and, where practicable, laboratory tests should parallel plant practice.

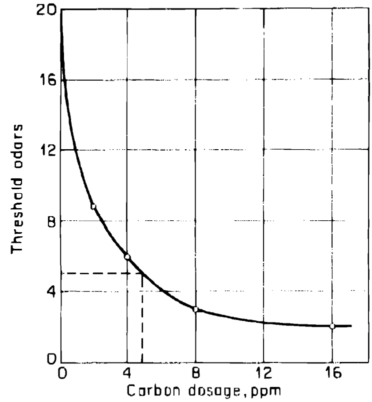

Fig. 1 Arithmetic plotting of results of Optimum Dosage test on water having initial odor concentration of 20.

Inasmuch as better treatment results are obtainable in the plant than in laboratory tests, the dosage first adopted for plant-scale application should be about half that indicated by the laboratory tests. If carbon has not been used in the plant for some time, and the plant is therefore not seeded with carbon, however, it is recommended that the full dosage developed in the threshold odor tests be employed in actual plant operation. This dosage can then be gradually reduced by trial and error methods until the optimum dosage is established.

Granular Carbon. Increasing demands for more palatable water coupled with lower regeneration costs for spent carbon have caused renewed interest in the use of granular activated carbon for municipal water

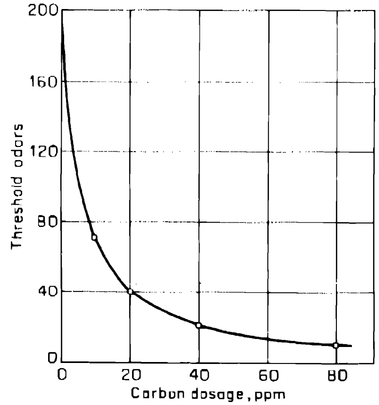

Fig. 2 Arithmetic plotting of results of Optimum Dosage test on water having initial odor concentration of 200.[17]

treatment. Pressure-type filters of granular carbon are used extensively by the bottling industry for quality control, and adaptations of such systems offer promise to smaller municipalities. Pilot plant studies[62] have successfully demonstrated that such carbon filters can simultaneously filter the raw water and remove taste and odor substances to produce a water of consistently high quality. For most plants, however, granular carbon filters are used in the form of carbon beds. These beds are normally placed after the conventional filtration system, but in cases where the water is relatively clear, the beds may be used without prior water treatment and clarification. Usually two or more beds are used in downflow parallel operation with staggered start-ups so that the adsorption capacity of each filter bed is eventually exhausted in sequence. Reactivation is accomplished by thermal treatment; total carbon losses upon reactivation normally amount to 5 per cent or less. Design parameters and the economics of granular carbon systems have recently been presented to demonstrate that granular carbon treatment compares favorably with powdered carbon treatment on an economic basis.[63] Plant studies using raw water that has severe taste and odor problems have been conducted in conjunction with these design parameters. Results[64] showed that the carbon beds were quite effective in removing specific chemical pollutants as well as lowering the amounts of organic matter (as measured by the carbon adsorption method) to recommended drinking water standards of 200 ppb.

PREVENTION OF TASTE AND ODOR

The foregoing material emphasizes the complexities involved in dealing with taste and odor in water. It is axiomatic that two basic requirements are essential for the constant prevention of taste and odor in drinking water supplies: intake sites should represent that best raw water quality for the area being served, and the best combination of appropriate treatment systems should be in routine practice to ensure both a potable and palatable water for the consumer. Likewise, it is evident that the complete cooperation of all the water users is necessary in order to fulfill these requirements.

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7a
Filtration

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INTRODUCTION

Filtration is defined as the passage of a fluid through a porous medium to remove matter held in suspension. In water purification, the matter to be removed includes suspended silt, clay, colloids, and microorganisms including algae, bacteria, and viruses. The particles to be removed have approximate sizes as follows, stated in millimicrons (a micron is 0.001 mm, and a millimicron is one thousand times smaller).

Material	*Particle size, millimicrons*
Silt	50,000
Bacteria	5,000
Viruses	50
Colloids	1–1,000

The Filter

As used in water treatment, a filter may consist of a thin porous layer of filter aid deposited by flow on a support septum, or a bed of granular nonporous material held in place by the force of gravity or by the direction of flow. The former is covered in detail in Chapter 7b.

The most widely used units of the latter type are rapid-sand filters in which gravity holds the material in place, and in which the flow is vertically downward. The filter medium is usually supported on a gravel bed which is underlain by an underdrain system that collects the water into a pipe which conveys it to a filtered water chamber.

Carefully screened gravel is usually installed in a series of layers several inches thick ranging from coarser stones at the bottom to 0.1-in. particles at the top. The coarse material absorbs the energy of the high-velocity jets emerging from the underdrain system, and the diminishing size is intended to serve two functions: (1) to spread the flow uniformly under the entire sandbed area during backwashing and (2) to support the sand so that it will not pass downward out of the bed during the filtering cycle. The filter is periodically cleaned with filtered water by reversal of flow and discharge of the sediment-laden water to a drain. Most rapid-sand filters are contained in concrete boxes and designed so that the upward flow of wash-water, with auxiliary scouring systems, lifts the removed sediment out of the expanded filter medium and flushes it away to a point of disposal. Figure 1 shows a typical rapid-sand filter of large size.

The filter media normally used in American practice are described by the following table:

TABLE 7–1 Properties of Filter Media Materials

Material	Shape	Density	Hardness*	Porosity, %	Range of effective sizes used, mm
Silica sand	Rounded	2.6	7	42	0.4–1.0
Silica sand	Rough	2.6	7	44	0.4–1.0
Crushed quartz	Angular	2.6	7	53	0.4–1.0
Silica gravel	Rounded	2.6	7	40	1.0–50
Garnet sand	....	3.1–4.3	6.5–7.5	.....	0.2–0.4
Crushed anthracite	Angular	1.5	3	55	0.4–1.4
Alluvial anthracite	Rounded	1.5	3	50	0.4–1.0

*Moh scale.

Sizes are normally determined by sieving, and usually expressed in terms of the effective size—the size particle which is exceeded in fineness by 10 per cent of the sample. The distribution of sizes is expressed by the uniformity coefficient, which is the ratio of the 60 per cent size to the effective size. For properties of diatomaceous earth filter media, see Table 7–2 in Chapter 7b.

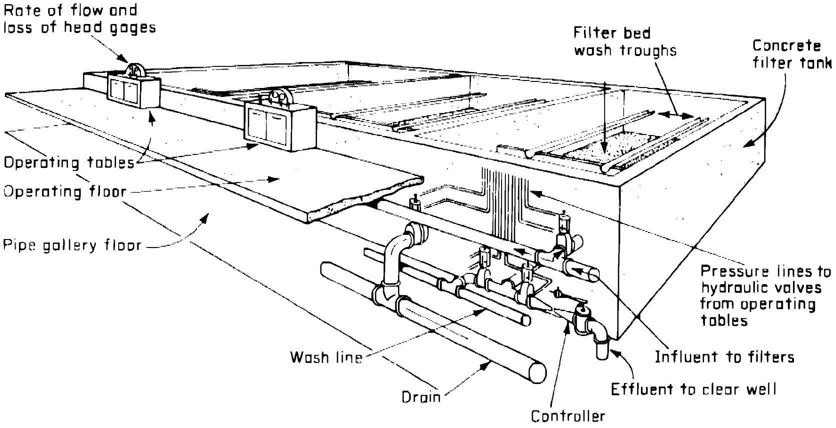


Fig. 1 Battery of three filters.

Pretreatment Effects

The traditional rapid-sand filter, containing sand of 0.5 mm effective size, 24 to 30 in. thick, operating at a 2 gpm/sq ft filtration rate, is not effective in clarifying water that has not received prior treatment. Figure 2, based on data from Chicago and Montreal, shows that rapid-sand filters operated on unflocculated water were unable to produce water meeting the USPHS drinking water standard of five turbidity units (Jackson units—j. u.) when the raw water turbidity exceeded 15. Because of this, flocculation of water prior to filtration is almost always employed. In most cases flocculation has been followed by sedimentation to reduce the quantity of material applied to the filter.

The most important characteristics of the flocculated water applied to filters are: (1) the completeness of the flocculation and (2) the strength of the flocs. If, due to deficiencies in plant facilities or underdosage of coagulant, the fine particles are not all entrapped in the floc, the filters will be unable to remove them. This will be so even with small-diameter media, low filter rates, thick beds, etc. Variations in such parameters have little effect on filter effluent quality when flocculation is insufficient. Because this so frequently happens, some observers have concluded that variations in these parameters are unimportant.

Sometimes that is so, but there are cases in which, though flocculation is complete, the flocculated matter penetrates through the filters. It lacks the strength or toughness to resist the shear forces that occur in a filter bed. When this condition occurs, sand size, porosity, bed thickness, filter rate, and other variables exert a profound effect on water quality, as will be discussed in the next section. For orientation in evaluating floc strength, the

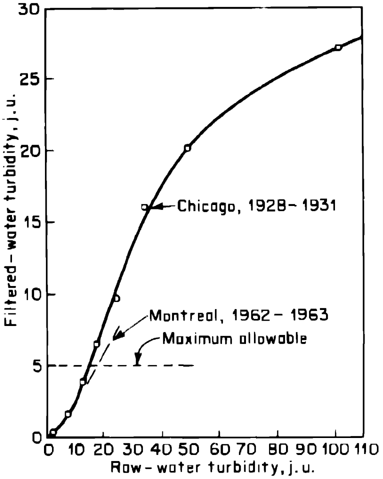


Fig. 2 Removal of turbidity by rapid-sand filtration without flocculation; 0.5 mm sand, 24-in. bed, 2 ppm/sf, Filter No. 12, Chicago, Oct. 1928–Sept. 1931.

following comparative table on 0.5-mm sand, 24 in. thick, 42 per cent porosity, and filtration rates of 2 gpm/sq ft is presented:

Floc strength	*Condition*
Very weak	Breakthrough begins when the filter sand head loss is less than 2 ft of water
Weak	Turbid effluent begins after head loss reaches 2 ft but before 8 ft of water
Medium	No breakthrough, but penetration of floc into bed greater than 3 in.
Strong	Penetration of floc into bed less than 3 in.

Weak flocculation may be caused by a chemical spill of a material like phosphate into the source. One such event occurred in the Detroit River in 1958 and lasted 5 days. All plants along the river were affected.

Lake Michigan water produces weak flocculation under characteristic circumstances. A strong north wind causes high turbidities at the southern end of the lake. With an increased coagulant dose, this water is easy to flocculate. As turbidity declines after the storm, weak flocculation ensues, requiring use of a flocculation aid for a period that may last from a week to a month. Certain rivers exhibit similar behavior after a flood.

Fortunately pretreatment techniques, including more intense mixing, reduction of short circuiting, and the development of flocculation aids have steadily improved in recent years. The following table illustrates recent trends in water treatment, including both pretreatment and filtration.

Year	Turbidity of applied water	Filtered water	
		Turbidity	Number of particles /ml
1920	30	5	10^7
1940	3	0.5	10^6
1960	0.3	0.05	10^5

THE FILTRATION PROCESS

Filter Behavior

The following description of the filtration process is based on observations of sand filters using an optical magnifier to watch floc particles and fine-colored tracer streams. Similar phenomena would be seen in other media, such as anthracite.

Floc particle size and strength are of basic importance to the filtration process. In the water applied to filters, floc particle size may range from 2 mm down to sizes less than 0.1 mm. In a filter containing rounded media, the pore opening sizes will range from 15 to 40 per cent of the particle diameter. Thus the pore openings in a bed of 0.5-mm sand will range from 0.1 to 0.2 mm in size. In coarse, angular media, such as 1.2-mm anthracite, because of greater porosity, pore openings are larger, ranging from 0.3 to 0.6 mm.

It follows from these dimensions that the larger floc particles can be removed by simple straining at the bed surface, but that much of the flocculated matter will pass into the bed and lodge within it. Unless the flocs are exceptionally strong, those that initially lodge in the bed by simple straining will subsequently break as the hydraulic gradient increases. Since breakage of the flocculated matter within the bed is inevitable, it is not necessary to handle settled water gently. Rough treatment, such as tumbling over weirs or pumping seems to have no adverse effect on filterability of the applied water.

The flocculated material in the water passes into the filter bed through thousands of openings in each square foot of the filter surface and, by the end of a filter run, ordinarily lodges largely in the top 1 to 4 in. of the bed. When a clean filter is placed in service, nearly all of the floc particles pass into the bed. As the flocculated matter lodges between the sand grains beneath the surface, the free void area is reduced, and the bed offers resistance to the flow of the water. Conditions then begin to change. The rate of flow increases through the larger openings and lessens through the smaller and partly clogged openings. As a result, many of the larger passageways remain nearly free of deposited material (Fig. 3). As filtration continues, the smaller openings become so filled with the coagulated material they are almost closed. The number of openings at the surface per square foot of filter area is still very large, and there may not be an area as much as ½ sq in. without a hole. Gradually many of these holes stop feeding channels when the voids beneath the surface become so clogged that flow becomes impossible.

At the beginning of a filter run nearly all of the floc particles lodge in the sand within ½ in. of the surface. Particles that impinge on previously removed flocculated matter adhere to it. The opportunities for lodgement or attachment are very large, for with 0.50-mm sand each drop of water that passes through the filter has to pass 3,000 or more small openings between the sand grains.

If the sand grains are small in size, or if the floc is tough, the penetration of flocculated material beneath the sand surface may be small. This is illustrated in Fig. 3*a*. Figure 3*b* represents penetration of part of the coagulated material into the bed with a fairly large portion of it remaining at the surface. Figure 3*c* depicts continuing penetration into the bed through channels. Figures 3*b* and *c* represent conditions which are expected to take place in a rapid-sand filter bed. These figures are diagrammatic; the channels are actually quite crooked. To obtain filter runs of reasonable length with sand beds, the penetration of coagulated material

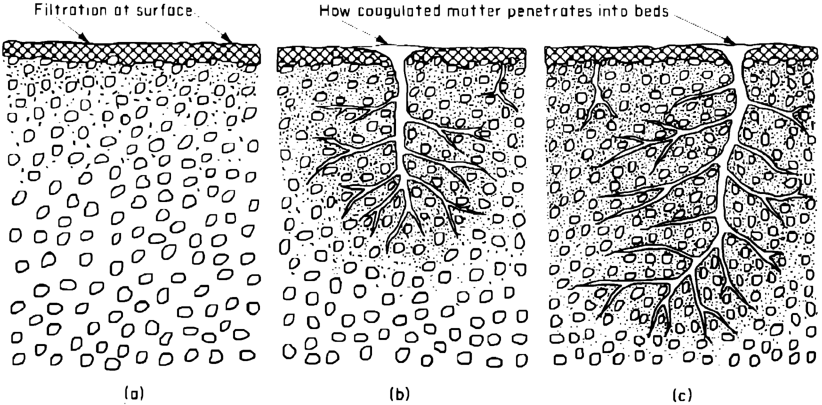


Fig. 3 Sketches showing what takes place in a filter bed.

into a single-media bed should be from 2 to 4 in. When there is little penetration of the material into the filter bed, as shown in Fig. 3*a*, the filter loss of head increases rapidly, and the filter runs are too short for practical operation of the filters. When penetration is greater, flocs pass down into coarser underlying layers, and there is danger of breakthroughs.

There is little or no deposition of flocculated material in the channels where velocities are high. The sediment-bearing water moves down the channels until it reaches voids that have not been filled with the coagulated material. It then spreads out, the velocity reduces, and lodgement of flocs again takes place.

When the voids in the sand around the end of a channel have filled sufficiently to increase the resistance to flow, previously deposited floc shears, and new channels open up through previously unperforated areas and conduct the water to unclogged sectors. These new channels are caused by the increasing hydraulic gradient, which causes increased shear stress. The process continues to repeat itself. As the loss of head through the filter increases and the flocculated material clogs to a greater depth, the channels through the surface become fewer. Some water also enters the bed by seepage through the surface layer. The part that does this is small in comparison to that entering through channels.

Figure 4 is a photograph of the surface of a filter when the head loss had reached about 8 ft. The water was filtered down to about 2 in. above the sand surface and the camera pointed straight downward. The holes shown in Fig. 4 are the type illustrated in Fig. 3*c*. There was no way of telling how deep the holes extended into the bed as channels of rapid flow, but some of them may have extended as deep as 2 or 3 in. or more, with resulting penetration as shown in Fig. 3*c*.

Figure 5 is a photograph of 2-in. glass tube filters. The 4-in. penetration of the coagulated material may readily be seen in the white sand bed. Penetration into the anthracite beds shows up to the eye, but not in the photograph. Results of a test of head loss and bed penetration during iron application, made by O'Melia and Crapps,[1] are shown in Fig. 6. Both head loss and penetration were affected by the anions present. Phosphates caused very weak floc, evidenced by rapid floc penetration and low head loss, while chlorides caused moderate penetration and high head loss (medium strength). A comprehensive review of physical aspects of filtration has been made by Mintz.[2]

The probability of a floc particle striking the surface of the filter medium is influenced by sand size, porosity, filter rate, temperature, and density and size of floc particles. The adherence of the particles is affected by colloid chemical forces which include the age of the floc, temperature, coagulant concentration, type and concentration of anions, and pH. There is general agreement that the understanding of the process of filtration

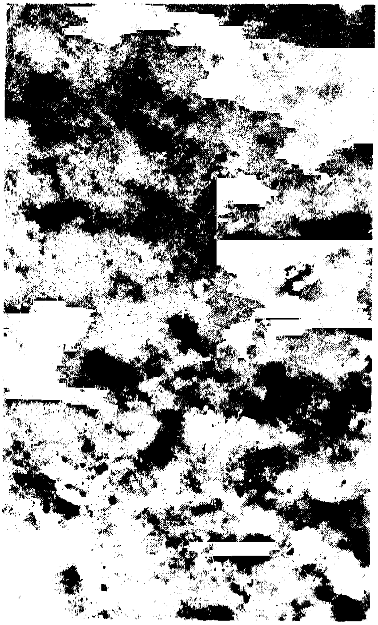


Fig. 4 Photograph of holes in filter bed.

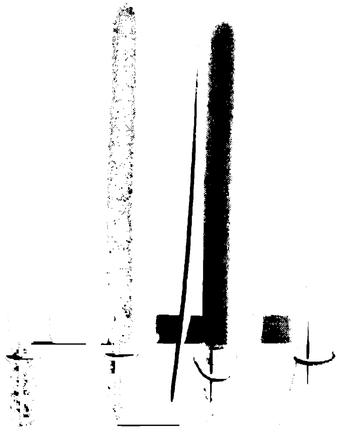


Fig. 5 Penetration of coagulated material into filter bed.

is at present too incomplete to permit prediction of filter performance without pilot testing.

Variables in the Process

Filter runs not less than 12 hr in length and preferably more than 24 hr are sought in order to free operators for other duties within the plant. With automation, shorter filter runs might be tolerated, but they increase the use of costly washwater and, through increasing "downtime," reduce plant production. In extreme instances, net plant output has been severely cut by extremely short filter runs. Contemporary practice commonly calls for backwashing filters at intervals no greater than 60 hr to keep them in good condition.

The American Water Works Association has established water quality goals which it states can be readily met. These call for reduction of turbidity by filtration to less than 0.1 j. u. Using careful pretreatment prior to filtration, and assisted by the monitoring devices, a number of plants in the United States have been routinely producing water having filtered water turbidity in the range of 0.02 to 0.07 j. u. By this means they are providing additional protection against the passage of bacteria, chlorine-resistant viruses, and colloidal particles that color the water and carry tastes and odors.

The relationships between the numerical values governing the design and operation of rapid-sand filters are approximated in the following observational equations:

$$C_e = f\left(V, d^3, p^4, \frac{H}{L}, C_0, S\right) \tag{1}$$

$$T = f\left(\frac{d^2\, p^4\, H\, S\, L'}{V^{1.5}\, C_0}\right) \tag{2}$$

in which C_e is the concentration of suspended material in filtered water;

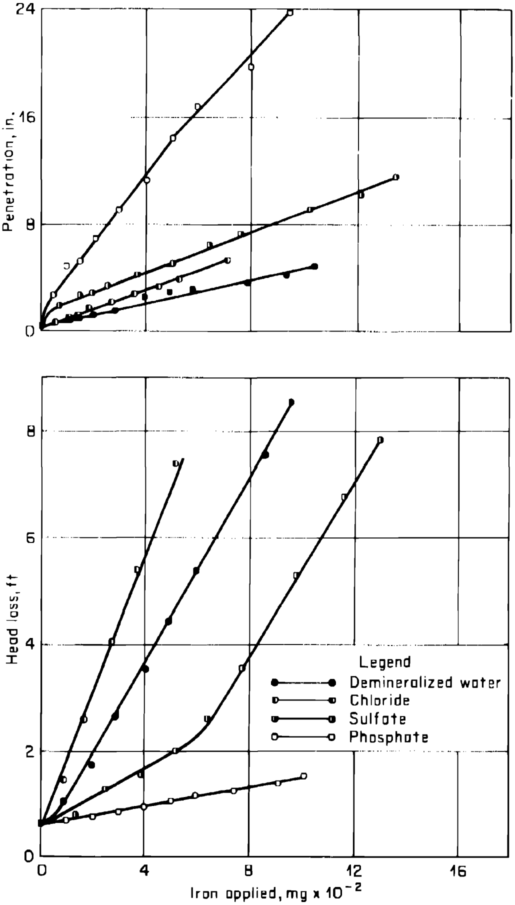


Fig. 6 Bed penetration and head loss versus total iron applied at pH of 0.7 during run 6.

C_0 denotes the concentration of suspended material in applied water; d denotes the effective size of filter media; p is the porosity of filter media; H is the terminal head loss through filter bed; L describes the depth of floc penetration in filter, weakest flocculation; L' denotes the depth of floc penetration in filter, strongest flocculation; V refers to the filtration rate; S is the surge amplitude; and T refers to the length of filter run.

It must be emphasized that Eq. (1) applies only to conditions of such weak flocculation that flocs can penetrate entirely through the bed. When penetration is small, C_e depends almost entirely on the completeness of flocculation in the pretreatment process.

Equation (2), on the other hand, is intended to apply to any conditions, but is most useful for the situation that causes the shortest filter runs.

Although the values to be used in Eqs. (1) and (2) may be derived from traditional design practice, it is preferable to develop them from operating records of existing plants or from pilot plant work. The values of C_e (concentration of suspended matter in effluent) and T (length of filter run) are set as design objectives: they may be considered as averages or as maxima.

The numerical values used in Eqs. (1) and (2) are less important than the relationships shown between the variables and the design objectives. For example, it is evident that, for a given floc strength, if increases in C_e are to be prevented, a contemplated increase in filtration rate must be offset by a corresponding change in one or more of the other variables and that each of these changes will cause a corresponding change in the lengths of the filter runs. Design factors such as sand size, porosity, or bed thickness, once established, are fixed; whereas others, such as filtration rate, terminal head loss, floc strength, and concentration of suspended matter in the applied water may be varied during operation.

Though neither precisely stated nor dimensionally consistent, these equations show how the design variables are related to the two principal design objectives: water quality and practicability, the latter determined chiefly by filter run length. The limiting values for these equations are obtained from separate sets of conditions. Equation (1) is evaluated during the period of greatest difficulty in production of clear filtered water. This is the time of weakest flocculation, and it ordinarily occurs when the water is cold. Equation (2) is evaluated during the period of most-rapid filter clogging. This generally coincides with the time of strongest flocculation and is usually in warm weather.

An increase in filtration rate causes a deterioration in filtered water quality and at the same time causes a proportionately greater reduction in filter run length.

The effects of filter-medium size, shape, and porosity on filter behavior have often been overlooked. Figure 7*a* shows the effect of particle size on filter runs for rounded sand and for angular anthracite. The coarser and

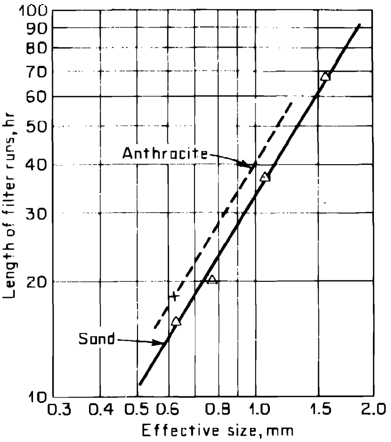


Fig. 7(a) Effect of filter medium size on filter runs; 3.2 ppm/sf (U.S) Alum Flocculation, Chicago, Feb. 1938–Jan. 1939.

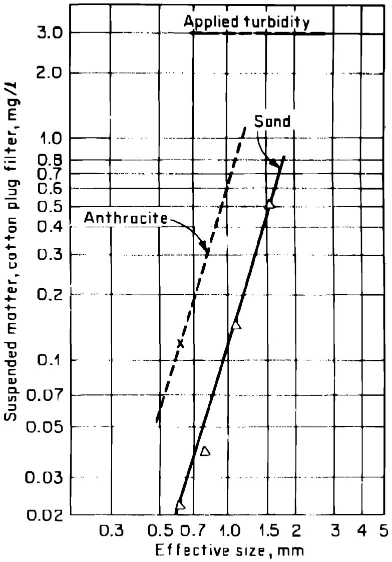


Fig. 7(b) Effect of filter medium size on effluent suspended matter; 3.2 ppm/sf, Chicago, Feb.–Mar. 1938.

more angular materials yield longer filter runs, but at a price, as Fig. 7*b* shows. In the latter figure the effects of porosity and size on water quality are illustrated. Though the gain in filter runs using coarser media is 40 per cent, the detrimental effect on filtered water quality is fivefold. In contemporary filters this behavior is increasingly recognized and utilized by using dual-medium beds with an underlying layer of 0.45- to 0.5-mm sand and a thick (18- to 30-in.) layer of anthracite of 1.0 to 1.4 mm effective size. The combination attains longer runs without sacrificing quality.

A number of plants have employed triple-medium beds with the insertion of a thin layer of fine garnet sand below the silica sand. This layer is in turn supported on a coarser garnet layer that rests on the gravel. The authors have not had the opportunity to evaluate the stability of this system in relation to gravel movement. There is, however, no doubt at all that the dual-medium system is superior to any single-medium bed in capability to produce longer filter runs and, perhaps, higher quality water. The evidence is so clear that there now is little justification for the use of single-medium beds.

Contrary to the restricted floc penetration desired for safety with single-medium beds, the dual-medium beds are designed to encourage complete penetration of the upper layer, but very limited penetration of the underlying finer bed. In dual-medium beds of 18 in. of anthracite and 12 in. of sand, penetration of about 1 to 2 in. into the sand may be allowable. Effective size of anthracite may be in the range 0.8 to 1.4 mm, and sand, 0.4 to 0.5 mm, depending on local minimum floc strength.

Increasing the terminal loss of head through the bed may cause a worsening of water quality, but it lengthens filter runs approximately in proportion to the increase in terminal head loss.

When flocs are strong, and there is little penetration into the bed, filter thickness has a negligible effect on the lengths of filter runs. On the other hand, when floc is weak, and filter runs must be terminated at low head losses to prevent breakthroughs, bed thickness has a marked effect on length of runs. Traditionally, bed thicknesses of 20 to 30 in. have been used for rapid-sand filters.

When flocs are weak, the concentration of suspended material in the filtered water is directly related to the concentration in the applied water. The application of a high concentration of suspended material to a filter causes increased floc penetration and an increased concentration in the filter effluent. The increase in applied concentration also causes a corresponding shortening of filter runs. When flocs are strong, variations in concentration have little effect on effluent quality.

The flocs in water applied to the filter may be strengthened by use of activated silica or polyelectrolyte coagulant aids. This strengthening, which may be sixfold or greater, can produce a great improvement in filtered water quality, but unless it also greatly reduces the concentration of suspended material in the applied water, strengthening the floc shortens filter runs.

The rapid-sand filter is one of the few engineering devices that permits direct sensing of momentary fluctuations in the overall flow. Such fluctuations are caused by boundary separations, eddies, etc., in the filter outlet piping, where the flow is turbulent. On the other hand, within the filter media the flow is laminar, and the amplitudes of transient head loss variations, or surges, therefore directly reflect momentary changes in the rates of flow through the filter medium.

These surges may readily be observed in a piezometer connected to the filter effluent piping system. They may reach amplitudes as great as 20 per cent of the mean flow rate when caused by "hunting" or erratic behavior of rate control equipment. Normally they are less than 6 per cent of the flow rate. The effect of surges has not been precisely evaluated, but Baylis has indicated that the quality of filtered water is materially impaired by them.

Control of Filter Operation

Since the mission of a filter is to separate suspended matter from the water, measurement of the remaining suspended matter concentration is essential. This matter is extremely varied: it may include bacteria, viruses, fine floc particles, uncoagulated colloids, clay or silt, color colloids, etc. Bacterial determinations, both of coliform organisms and total bacteria, are essential and should be made routinely to confirm the effectiveness of operation; however, since they require time for incubation, they have little value for the quick determination of need for treatment changes. Residual coagulant determinations are also valuable, but they are not easily made and also take some time. The cotton plug filter does a precise job of averaging the suspended matter concentration over a period of days, but it contributes nothing to the minute-to-minute control needed.

The most useful criterion for control of treatment operation is turbidity. This may be measured on samples in laboratory turbidimeters, but there are two more-rapid measuring methods available for control of operation: (1) the illuminated sightwell, and (2) the continuous-flow light-scattering nephelometer.

A simple sightwell arrangement is shown in Fig. 8. With experience, a turbidity of 0.01 j. u. can be detected by eye. An access opening is provided for servicing the submerged light. The observer looks for particles alongside the light, using the Tyndall effect. This type of sightwell is a

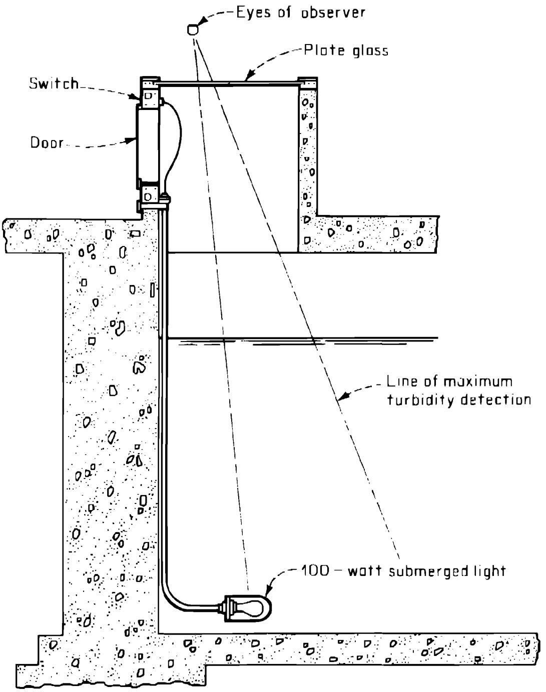

Eyes of observer
Plate glass
Switch
Door
Line of maximum turbidity detection
100 – watt submerged light

Fig. 8 Submerged light for turbidity detection.

valuable aid to the plant operator to tell him when turbidity is passing the filters and there is need for adjustment in chemical treatment or filter control.

A more refined sightwell has been developed. It consists of a vertical cylindrical still well about 18 in. in diameter, projecting from above the operating floor into the filtered water chamber to a level below the lowest filtered water level. A glass covers the top, and a submerged light is provided, located outside the field of view through the cylinder, mounted on a vertical track below an access door, for servicing. The light is a sealed beam unit which projects a concentrated beam horizontally through the water across the line of sight through the sight tube. The floor of the chamber in the field of view is covered with black and white tiles laid in a checkerboard pattern. The white tiles convey the impression of cleanliness, and the black ones provide the desired dark field. This sightwell is even more sensitive than that shown in Fig. 8 and functions well with any depth of water. Provision is needed to remove accumulated air bubbles or other materials that may get trapped in the well.

A number of continuous-flow light-scattering microphotometers are now available for water utility use. The better types are sensitive to 0.001 and dependably accurate to 0.005 j. u. In general, the surface-scatter type is preferable because all electrical components are above water and readily accessible. Because of certain practical problems, the units having 90° scatter are preferred. All are provided with indicating equipment, but the recording type is preferable in that it gives a visual presentation of trends.

In some plants, sampling taps from a number of filters are manifolded into a header leading to the turbidimeter. The lines are controlled by solenoid valves, and a sequencing switch automatically rotates the source of supply to the turbidimeter from one filter to the next. It is of great importance that the sampling lines are air-free. If a sampling pump or siphon is used, or if there are rises in temperature, an air separation chamber may be required to eliminate bubbles, which cause false turbidity readings.

Operators accustomed to using the continuous-monitoring recording filtered-water turbidimeters quickly notice departures from normal. They recognize the effects of operations such as basin shutdowns, filtration-rate increases caused by defective control devices, taking filters out of service for washing, coagulant underfeeds or interruptions, improper alkali dosages, changes in raw water character, changes in floc strength, etc. Initial and final filter breakthroughs also show up conspicuously. By seeing the effects of these phenomena, operators learn to anticipate, prevent, control, or correct them. This new knowledge and awareness helps to make feasible the operation of water-treatment plants at increasingly higher rates.

Figure 9 gives an illustration of the behavior of a filter during a filter

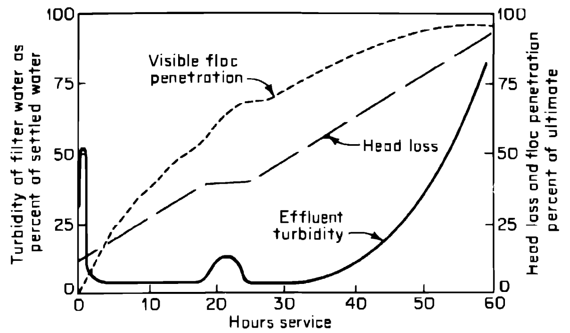


Fig. 9 Behavior of filter during filter run.

run. It shows the initial breakthrough, a transitory jump in effluent turbidity, and a terminal breakthrough. Since initial breakthrough usually lasts no more than 30 min, and therefore has no great effect on the general plant average quality, in most plants no corrective action is taken. In some plants water is filtered to waste for 15 to 30 min at the start of each filter run. British waterworks practice usually includes a 30-min slow start for each filter run as a measure to prevent the initial breakthrough.

The transitory turbidity jump at 20 hr (Fig. 9) is the kind of event caused by a coagulant underfeed or failure. It shows up quite conspicuously on a recording effluent-turbidity monitor. The turbidity rise at the end of the run, occurring as floc penetration approaches the full bed depth, is typical of the terminal breakthrough caused by a condition of weak flocculation. To detect such conditions, it is helpful to have a turbidity monitor on an individual filter as well as another on the total plant production.

When there are breakthroughs due to weak flocculation, and when they cannot be corrected by chemical means, good operating practice requires termination of filter runs at head losses lower than 8 ft, and reduction of filtration rate also helps. The example shown in Fig. 9 would have called for backwashing when the head loss reached a little more than half of the usual maximum, or at about 4 ft, or for a reduced filtration rate.

Control of Filter Flows

There are two general schemes of control of filters: control of the rate of flow and control of the head loss. The former has traditionally been designed into gravity rapid-sand filtration plants in North America, where the design rate has been 2 gpm/sq ft average, with hydraulics permitting a 50 per cent overload. For this system, each filter is provided with a pressure-differential-sensing device and a throttling valve. These elements are interconnected either directly or through a power boosting system (hydraulic, pneumatic, or electric) so that the filter automatically produces the selected flow rate until its loss of head approaches the total available head (difference between applied water level and the level of the filtered water outlet).

Frequently this system is used as described, and the plant operator has to select and regulate: (1) the plant inlet flow rate, (2) the filtration rate, and (3) the rate of discharge to the distribution system. Operators often vary filtered water production by starting or stopping units to keep the job simpler, though this practice fails to take advantage of the somewhat better water produced at lower rates, when flocs are weak.

There are filter master control systems which automatically increase the "set point" for the individual filter controllers in order to maintain uniform applied water levels. Another variant is adjustment of the set point in accordance with the filtered water storage level. These eliminate one of the choices required of the operator.

Another type of design is one that hydraulically forces the filters to accept and treat whatever water is sent to them. In one form of this, water enters each filter over a weir. A level-sensing device within the filter is used to regulate the filter effluent valve, either directly from a float or through a power system. Another form of this system lets the filtered water leave the filter over a weir. Applied water enters the filter over a weir and, at the start of a run, assumes a level not far above the filter media, then gradually rises as the run progresses until the inlet weir level is reached. The unit is then backwashed.

A third system, called "declining-rate" or "controlled-head" operation, connects all filter effluent lines to a common header. The pressure in this header is raised or lowered to reduce or increase the production of all the filters simultaneously. A fixed restraint, such as an orifice, is built into the effluent piping for each filter so that no filter, after washing, will take an undue share of the flow.

For example, for a group of filters operating at an average rate of 2 gpm/sq ft, the orifice will be so designed that a recently cleaned filter will begin operation at 3 gpm/sq ft, while the filter next in line for backwashing will have slowed down to about 1 gpm/sq ft. The filtered water header pressure may be regulated by a throttle valve which discharges to a filtered water reservoir, or the header may feed into an equalizing chamber from which the high lift pumps draw directly. The declining-rate system reduces terminal breakthroughs, saves head, automatically follows the high lift demand, and provides inherent master control for all filters.

First used in the United States on slow-sand filters at Albany by Allan Hazen in 1899, declining-rate operation is in successful use at a number of rapid-sand filtration plants built in the United States since the system was first tested from 1957 to 1958 at Wyandotte, Michigan. It was tested at

Chicago, using 20 filters in the South District Filtration Plant, from October 1958 through May 1959. No significant difference was found in the quality of water produced by the declining-rate filters and by filters controlled by conventional rate controllers. However, as Fig. 10 shows, the declining-rate units produced 40 per cent more water per day than the conventional units when operated so that filter run durations were equal on both types.

Filtration rates higher than the traditional 2 gpm/sq ft value have been employed in many plants throughout the United States in the period following 1945. One of the best-documented examples was at Chicago, where twelve full-size filters in the South District Filtration Plant were successfully operated at fixed rates of filtration of 2.0, 4.0, 4.5, and 5.0 gpm/sq ft for a 20-yr period.[3]

Problems were encountered. The first problem was the loss of head through the filters, including the underdrain and rate control systems. Fortunately the plant hydraulics at Chicago permitted the higher rates. The second problem was preventing passage of flocculated matter through the filters at higher rates. Coagulant aids have done much to overcome this. Since peak loads are encountered mainly during the summer period, the temperature effect was minor, but the presence of algae and plankton organisms caused short filter runs at times.

The following conclusions were reached by the Chicago experiments.[3,4]

1. In filtration plants where a coagulant aid may be used during periods of weak coagulation, sand filters will produce a satisfactory quality of water operating at a rate of 4 gpm/sq ft of sand surface.

2. Bacterial loading can be greatly reduced by adequate prechlorination or other means of disinfection.

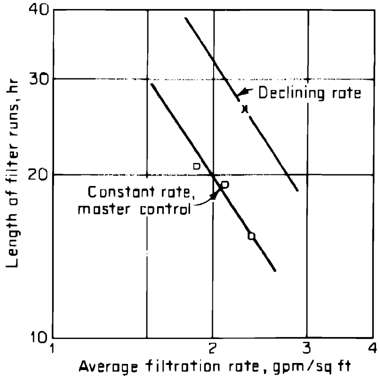


Fig. 10 Relation between lengths of filter runs and filtration rates, South District Filtration Plant, Chicago, 1959.

3. Doubling the filtration rate decreased the length of the filter run an average of 45 per cent. This meant that more water was filtered between washes.

4. The better performance for the high-rate filters indicated that the coagulated material penetrates deeper into the filter bed. This also meant that high-rate filters could pass flocculated matter at a lower loss of head than filters operated at 2-gal rate, particularly during periods of long filter runs.

5. Most surface water supplied in the northern climates requires the use of a coagulant aid or strengthening agent, especially during certain winter months. This is the period of the least requirement for high-rate filtration. During the summer months when higher filtration rates are required, the shear strength of the floc is greatly increased by microorganisms.

6. In the use of higher filtration rates, more attention should be given to the quality of water produced. Investigations at Chicago revealed that much of the reduced capacity of water distribution piping, formerly attributed to rust tubercules, was actually caused by the small amount of coagulated material that passed through the filters and coated the walls of the pipes, causing roughness.

Negative Head and Air Binding

Some filtration plants have only 4 to 5 ft of water above the sand surface and have occasional problems of air binding. Air dissolves in water at or near the saturation point. When the pressure is reduced to less than atmospheric pressure below the surface of the sand, air comes out of solution, and air bubbles accumulate below the sand surface, rapidly increasing the resistance to flow through the sand bed. Maintaining a high level of water above the filters reduces the head at which air begins to accumulate in the sand. Air binding in filters causes sand loss at the start of the backwash due to violent agitation from the entrapped air and requires that the filter must be washed before it reaches its normal time of service. In many water plants, air binding occurs only during the spring season when the surface water is in the stage of "warming-up" and is supersaturated with air.

CLEANING THE FILTER

When a filtering cycle has been concluded because of the development of a head loss so high that the filter can no longer produce water at the desired rate or because of depreciation of effluent quality due to terminal breakthrough, it must be cleaned. This usually involves: (1) closing the inlet valve, (2) filtering down to near trough level, (3) closing the filtered water effluent valve, and (4) opening the drain valve. Step 2 is sometimes omitted when there is need for haste. The filter is now ready for washing.

In some plants filters are cleaned by backwash alone, while in others surface-wash agitation is also used. Most European plants use an upward air scour together with a reduced backwash rate, but the success of this process seems to be greatest when the filter medium is coarse sand—0.8 mm in size or larger. Such coarse sand is seldom used in the United States.

The Washing Process

As the backwash valve is opened, the sand surface rises and a heavy concentration of coagulated material previously filtered from the water begins to overflow the washwater troughs and drains out the waste pipe. Within 3 or 4 min the water clears sufficiently for the backwash to be terminated. If the washing is continued a little longer, the surface of the sand may be seen, first dimly then very clearly, within 30 to 60 sec. At this time the sand level is some inches above its original level and is in vigorous agitation, boiling up in some areas. At the same time there is rapid and erratic lateral movement in some areas and slower movement elsewhere, first in one direction, then another. The movement is much more rapid than can be accounted for by the calculated average upward velocity of the backwash water.

Repeated observations of filter backwashing in a glass-walled filter having 10 sq ft of sand surface have shown that, with slow opening of the backwash valve, the sand bed gradually expands, beginning at the top of the bed, then progressing downward. When the backwash valve is fully open, the sand surface rises to its maximum height during the backwashing period. This may be from 3 to 12 in. or more above the original sand surface, depending on the sand size, rate of backwash, and water temperature. The rate of backwash for the large filters at Chicago, which contain 0.65- to 0.70-mm sand, is set to produce 3 to 4 in. expansion of the sand bed. Usual backwash rate is 15 gpm/sq ft. Higher backwashing rates are used in many filtration plants. The lower bed expansion is successful at Chicago because the surface wash is used as an aid in cleansing the sand, and a higher backwash rate with greater sand expansion is not necessary.

As backwashing begins, the sand grains do not move apart quickly and uniformly throughout the bed. Time is required for the sand to equilibrate at its expanded spacing in the upward flow of washwater. If the backwash is turned on suddenly, it lifts the sand bed bodily above the gravel layer, forming an open space between the sand and gravel. The sand bed then breaks at one or more points, as shown in Fig. 11, causing sand boils and subsequent upsetting of the supporting gravel layers. This then requires frequent rebuilding of the gravel section.

It is essential that the backwash valve open slowly. The time from start to full backwash flow should be at least 30 sec and perhaps longer and should be restricted by devices built into the plant. This is frequently done

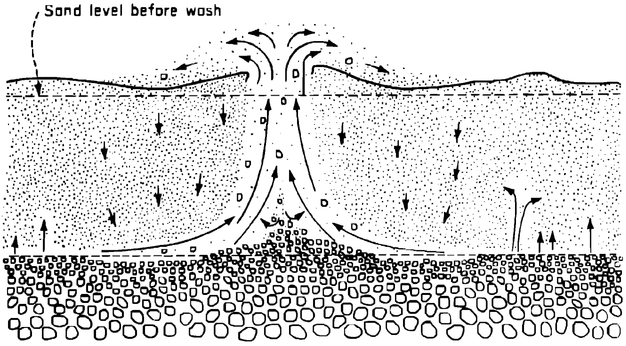


Fig. 11 Sand boil at beginning of wash.

by means of an automatically regulated master wash valve, controlled hydraulically or electrically and designed so that it cannot open too fast. If, in a given plant, such a valve cannot be provided, a speed controller should be installed on the operator of each washwater valve.

The most destructive filter washing blunder is to turn the backwash on quickly when the bed has been drained. Gross gravel disturbance results and rupture of the filter underdrain system due to water hammer has resulted in many cases, particularly with false-bottom–type underdrains.

The surface wash, commonly used in plants where the backwash cannot completely clean the filter, is of two types: the fixed-jet system and the filter-sweep type. Ordinarily both employ jets of about ⅛ in. diam, discharging at an angle of 15 to 30° below the horizontal, operating at pressures of about 75 psi. The jets are ordinarily located about 2 in. above the unexpanded sand surface. The filter sweeps are designed to discharge about 0.5 gpm/sq ft, while the fixed-jet type uses 2 to 4 gpm/sq ft.

A filter sweep is served by a vertical pipe bringing high-pressure water downward in the filter box. This pipe terminates in a swivel fitting, out of which project two horizontal pipe arms at 180° positions. Nozzles on one side of one arm and on the opposite side of the other cause the sweep to rotate when the flow is turned on. A typical fixed-jet system is shown in Fig. 12.

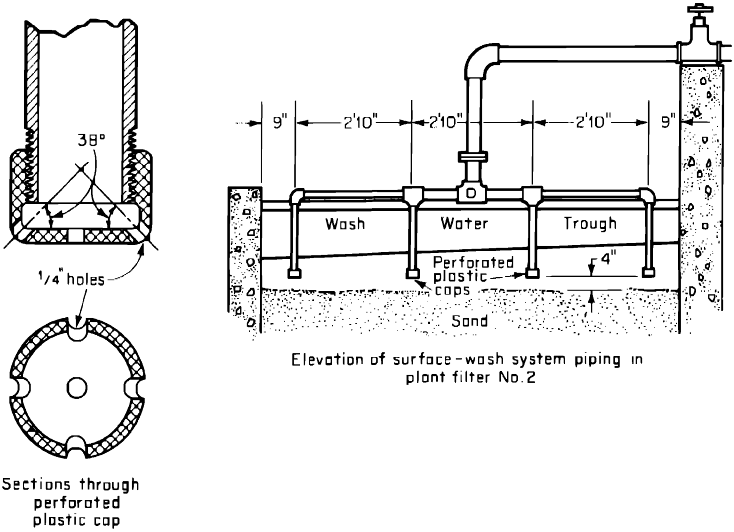
The surface wash is normally turned on before the backwash, and frequently a rate of wash that will barely expand the sand bed is used for several minutes to allow the surface wash to work hard on the top of the bed where mud balls form. This is then followed by a few minutes of higher backwash to flush out the bed. When the surface wash is used with anthracite, it is important to expand the bed to a level well above the jets. It has been observed that anthracite is more easily thrown out of the filter by the surface wash turbulence than is sand. Expanding the coal beds above the surface wash seems to reduce the loss of coal.

Mud balls sink more easily in anthracite beds than in sand beds and tend to form or accumulate at the coal-sand junction. To offset this characteristic, there is a trend toward installation of the supplemental wash system within the coal bed at an elevation about 6 in. above the sand. This requires check valve nozzles to keep the media out of the nozzles.

Jet Action

Just as channels form in the sand bed during filtration, the upward flow from the gravel is never completely uniform and, as a result, in some parts of the expanded sand bed the water and sand travel upward at rates higher than the average backwash velocity, and at other places the sand actually travels downward. Even with the most careful gravel selection and placement the gravel is disturbed in some degree by a natural tendency toward channeling. This leads to jet action at the sand-gravel junction, as illustrated in Fig. 13.

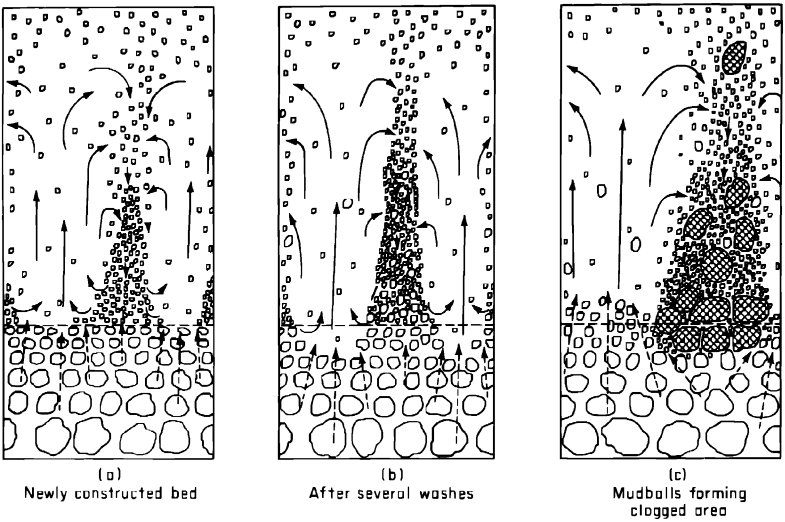
Jet action is a natural phenomenon which takes place wherever water flows upward through porous material with a velocity that partly suspends the material. It occurs wherever fine particles overlie coarser ones, and the upward velocity of the water partially expands the fine material but not the coarse. The size and specific gravity of the material merely affect the veloc-



Sections through perforated plastic cap

Elevation of surface-wash system piping in plant filter No.2

Fig. 12 Details of fixed-jet surface-wash piping.


(a)
Newly constructed bed

(b)
After several washes

(c)
Mudballs forming clogged area

Fig. 13 Jet action at the sand-gravel interface.

ity and the size of the jets and not their occurrence. The jet action is readily observed in a glass-walled filter.

An upward flow through a graded gravel bed at backwash rates exceeding 25 gpm/sq ft will not move any of the gravel particles unless sand is present on top of the gravel. The presence of the sand greatly increases the mobility of the gravel.

The head loss through an expanded 24-in. sand bed is approximately 2.0 ft, which corresponds to the weight of the media minus the weight of the water it displaces. Such a pressure beneath the sand has enough energy to cause localized flow velocities of about 10 fps, a flow rate 300 times greater than the average backwash rate. Such velocities can be very mischievous in a filter.

In some cases the jet velocity is so great that it will move small gravel particles several diameters larger than the sand grains adjacent to the gravel. With a normal backwash rate, the average upward velocity of the water through the gravel should be less than 0.1 fps. The velocities of the jets have been observed to be more than 10 times the average upward velocity through the area occupied by the sand.

Each jet must be fed with sand, so there is a downward or lateral movement of the sand around the jet. In a sand jet the sand occupies about 10 to 15 per cent of the volume of the sand and water. Where it is falling, the sand occupies about 30 per cent of the volume. The resulting difference in density between these two adjacent mixtures provides the force that sustains the rapid velocity in the jet.

These jets of water and sand are constant disturbers of the fine-gravel layers, and since the vast majority of filter beds are gravel-supported, the jets are a prime cause of the need for filter rebuilding. The jets cause lateral displacement of the gravel. This lateral movement is much greater when backwash rates exceed 15 gpm/sq ft. Sometimes several minor adjacent jets will merge to form a single stream operating at a high enough velocity to carry it to the top of expanded sand. There the boil may appear to be 12 in. or more in diameter. It generally occurs in the same place at each backwashing. Such a boil moves very coarse gravel and usually presages a failure to support the sand. See Fig. 14.

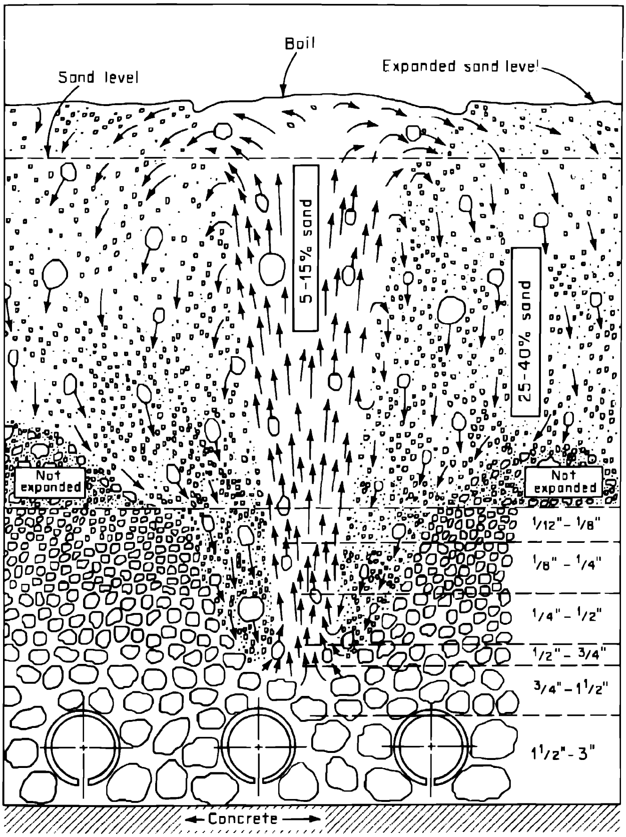


Fig. 14 Diagram of sand boil in filter bed.

In some instances, jet formation is stimulated by uneven distribution of backwash water; the jets tend to form where the backwash rates are higher. When this happens, a peculiar phenomenon occurs: the displacement of the gravel allows sand to pass downward into the underdrains, clogging them so that the area of originally high backwash rate becomes one of very low flow. The areas of jet formation then migrate laterally to new areas of high upflow, and ultimately a nearly complete reversal of the jet pattern predicted by hydraulic computations is found.

Probing the Gravel

To determine whether there is serious gravel movement, filters should be probed annually or more frequently if there is reason to be suspicious. There are two methods used: (1) with a ¼-in. metal rod while the filter is at rest, and (2) with a special probe during backwashing. The former procedure can be carried out with the water level at its normal elevation, at trough elevation, or with the filter drained. Either the water surface or the sand surface is used as a reference point. If the sand surface is not almost perfectly level, uneven distribution must be assumed. The gravel is probed on a horizontal grid system, depths to gravel recorded, and a contour map can be drawn if desired. Figure 15 shows 2-in. contours of a badly upset gravel bed. Gravel levels varied from 12 in. lower than the original level to 10 in. higher. This condition was followed by discharge of the sand into the filtered water reservoir.

For probing during backwashing, the thin rod may be used, or a special sounding device may be employed. This uses a steel or aluminum pole equipped with a 6-in. circular heavy-grade ¼-in. mesh screen welded to the end of the pipe or rod. The pipe should be of sufficient length so that the person making the test can stand in the washwater trough and conveniently measure the depth to which it penetrates. This is usually done using a low backwash rate that is sufficient to suspend the sand so that in probing, the screen rests on the top gravel layer. With such a probe, the check of the gravel layer height in the filter is usually made at intervals of several feet along each washwater trough.

Sand Leakage Detector

When there is a gravel failure, filter sand appears in the clear well. The sand detector (Fig. 16) was developed to identify the particular filter that was passing sand. One of these devices is attached to the bottom of each filter effluent piping just as it leaves the filter. If there is sand leakage, sand will deposit in the glass cup. These units are inspected once a week, cleaned if they contain sand, and a record made of the quantity found. Filters that have been in service for a number of years sometimes pass sand for a short while and then stop. If the passage of sand increases over a period of time, it is apparent that the gravel layers have been seriously upset and it is necessary to rebuild the filter media or correct any other trouble that may be the cause of the sand leakage.

Regrading Gravel

Figure 17 shows a conventional grading of gravel and a revised gradation developed at Chicago to prevent gravel movement. Behavior of this system was watched in a glass-walled filter. At 80 gpm/sq ft there was no movement of any of the gravel particles. It is safe to assume that the gravel could not be disturbed in normal washing. With the revised gravel arrangement, sand fills the voids in the 5-in. coarse gravel layer, in which the jets that form are very close together, and velocities are well dissipated by the entrained sand. During filtration, sand moved down into the gravel, but does not appear to reach below the ½-in. size. Complete conversion to this new gradation in every plant is not advocated; it should be tested out for a year or more in one unit.

A number of the filters at Chicago have been converted to this gradation and have given excellent service for more than a decade. Should there be clogging of the fine gravel with flocs or precipitates from softening operations, the bed can be cleaned with acid or alkali solutions, as required.

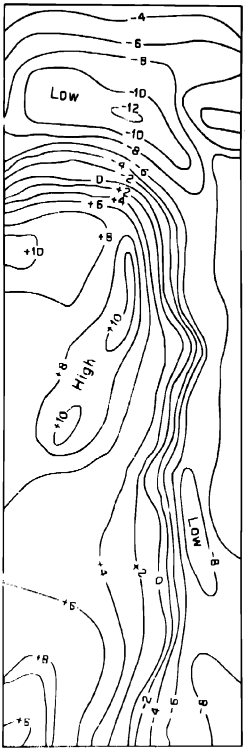
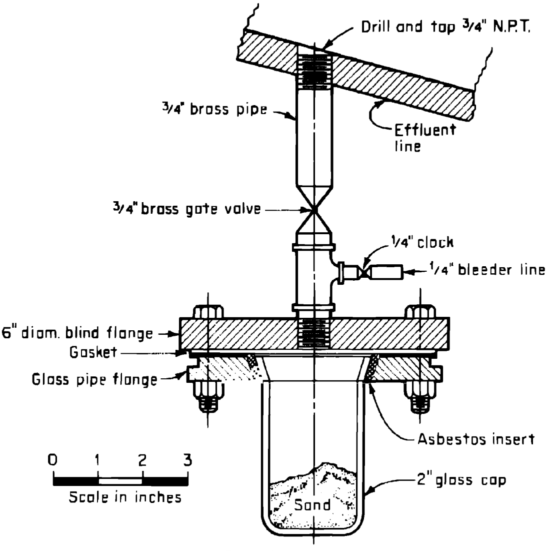


Fig. 15 Contours of gravel. The contours shown were typical of all filters in this plant. Contours are in inches above or below original gravel level.

Mud Ball Concentration

In all plants a periodic check should be made for the accumulated mud ball concentration. Where experience shows that the mud ball forming tendency is low, the check may be annual. Where the problem is severe, a monthly check may be desirable. In the early stages of filter deteriorations, the concentration of mud balls is greatest in the top of the bed. The mud ball determination is therefore made on the top 6 in. of the bed.

The sample for the mud ball determination is obtained with a sampling tube of thin metal about 3 in. inside diameter and 6 in. inside length, with



Sand-leakage detector

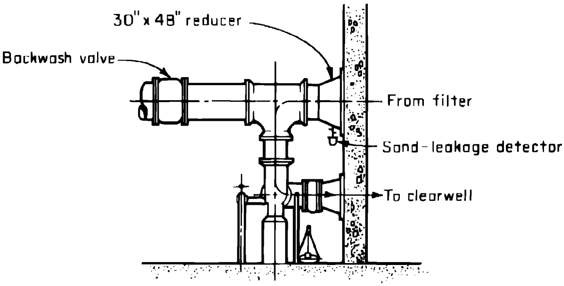


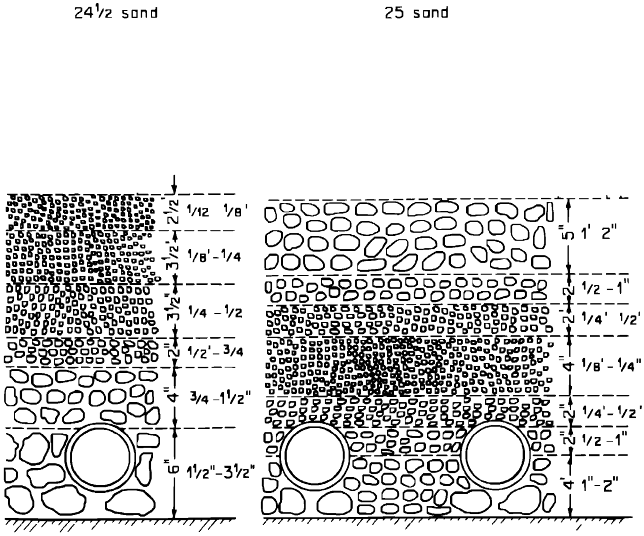
Fig. 16 Effluent piping showing location of sand-leakage detector.

a handle for convenience in handling, as illustrated in Fig. 18. The volume of this tube is such that five fillings of the tube give a volume of $\frac{1}{4}$ cu ft. After washing the filter to be sampled, the water is drained to at least 12 in. below the surface of the sand; then the tube is pushed down 6 in. into the sand, tilted until the handle is nearly horizontal, and lifted full of sand. This process disturbs the sand around the sampling location, but the sample is undisturbed. Since the sand is moist, the tube stays full of sand. Collect portions from five places in the bed, placing the portions in a bucket, so that the combined sample will be representative of the entire top 6 in. of the bed.

A 10-mesh sieve is used for separating the sand from the mud balls. It will normally pass all the filter medium and retain all significant mud balls. Hold the sieve in a bucket of water so that the sieve is nearly submerged. Put a handful of sand in it. Gently raise and lower the sieve about ½ in. at a time until all of the sand is washed through. Figure 19 shows mud balls retained on a sieve after washing the sand from the collected sample.

Do not place too much sand on the sieve at one time, as this may break up some of the softer mud balls and cause them to be washed through the sieve. Move the mud balls to one side of the screen by tipping the sieve to an angle of 15 to 20° while partly submerged, and gently oscillate it. The motion should be sufficiently rapid to separate the mud balls from the loose sand. Keep adding sand and washing through the sieve until the entire sample is sieved. If the concentration is high, it may be necessary to transfer mud balls to the measuring cylinder once or twice before the sample is sieved.

Measure the volume of the mud balls by displacement of water in a graduated cylinder (Fig. 19). The size of cylinder graduate depends upon the



Chicago filters New design

Fig. 17 Gravel depths in old and new designs.

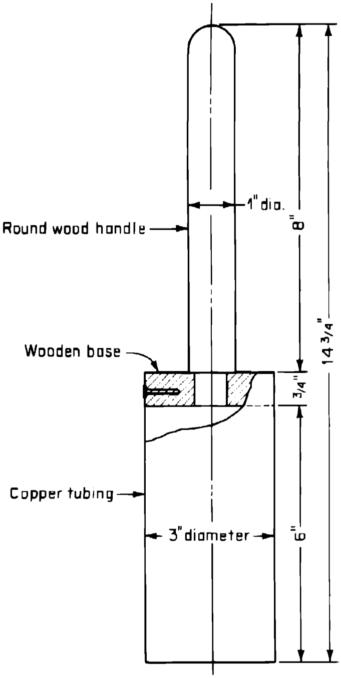


Fig. 18 Sand sampler.

volume of mud balls to be measured. Fill the graduate with water to a definite mark. After the water has drained from the mud balls on the sieve, transfer them to the graduate. Read their volume, which is the increase in the volume in the cylinder, and compute the per cent volume present in the sample. If, for example, the total quantity of sand and mud balls collected has a volume equal to that of a 6-in. cube (3,540 ml), and the volume of mud balls determined by measurement is 116 ml, the volume of mud balls is 3.28 per cent of that of the sample.

The classification in the following table for the top 6 in. of the filter is used at Chicago and is based on tests of filters in numerous plants.

Per cent volume of mud balls	Condition of filtering material
0.0–0.1	Excellent
0.1–0.2	Very good
0.2–0.5	Good
0.5–1.0	Fair
1.0–2.5	Fairly bad
2.5–5.0	Bad
Over 5.0	Very bad

The filter plant operator should strive to keep mud balls down to less than 0.1 per cent of the volume of the top 6 in. of the sand or other filtering material. Where the percentage volume of mud balls exceeds 0.2 per cent, extra facilities for washing the filters should be provided, such as a surface wash.

Because anthracite has a low density, mud balls sink more readily than in sand beds. Sampling the top 6 in. of an anthracite bed may not tell the full story. Here it would be better to sample the bottom 6 in. of the anthracite, and an appropriate modification of the above procedure would be needed.

PROBLEMS CAUSED BY DEFICIENCIES IN WASHING

Poor filter bed condition has often been due to neglect, but in some instances the neglect had a plausible rationale in the belief that sand coated with a gelatinous film is more effective than clean sand in removing impurities from water. This concept was a hangover from the early days of slow-sand filtration. Until about 1935, filter designers sought gentle rather than vigorous agitation of the sand during the washing process in order not to disturb the gelatinous coating around the sand grains. It is now known that such a coating has little value, and that it is readily removed with good backwashing. A thin coating does, however, assist in removal of iron or manganese. Except for problems caused by uneven distribution of washwater and improper grading of the filtering materials, nearly all filter bed trouble is attributable to failure of the washing process to remove from the filter the material that has been filtered from the water.

Fig. 19 Equipment for making mud ball volume measurements.

Fig. 20 Mud balls on filter surface.

Formation of Mud Balls

With deficient washing, the compacted material accumulates in the bed and grows increasingly compact. The particles grow to larger size by adhering to each other and to sand grains at the surface of the bed. Newly formed mud balls remain at the filter surface when the washwater is cut off, as shown in Fig. 20.

The mud balls grow increasingly compact and eventually reach a density great enough to cause them to sink into the sand during the washing period. While they are forming and being compacted, they are also being worn away gradually by abrasion by the sand during the washing periods. Some of them clump together in the bed and form mud deposits at the bottom of the sand bed or against the sidewall of the filter. If the rate of wearing away is as great as the rate at which the mud balls are built up, the volume of mud balls in the filter does not increase.

The rate of wearing away of clogged masses and mud balls is fairly uniform throughout the year and from plant to plant, but the rate of mud ball formation varies greatly from place to place and from time to time. In many plants, the concentration of mud balls in the filters diminishes in winter.

After a filter run it may be noted that some of the material filtered from the water is not removed from the filter at the usual rate of backwashing.

Part of the mud or coagulated material has become compacted during filtration. While the density of the compacted particles is less than that of the sand grains, the particles are much larger, and this gives them a settling rate through water nearly as great as that of sand. If the mud particles are not broken up by an agitating force much greater than that produced by backwash alone, these particles are not removed.

Bed Shrinkage During Filtration

When the sand grains in a filter are clean, they rest directly against other grains in the bed, and unless there is some vibration of the filter, there will be little compacting of the bed as the loss of head increases. If the sand grains are covered with a soft coating, the bed compresses as the loss of head increases. Cracks may form as shown in Fig. 21.

Measurements of vertical compaction have been made in a number of filter beds. The measurements were made with a light vertical rod supported by a flat base on the sand surface, placed after each wash. Movement of the rod was periodically measured from a reference point at the top of the filter. The curves show the progress of bed compaction as the head loss increases.

The upper line in Fig. 22 shows what happened when the sand grains had a fairly thick coating. The middle curve shows the settlement of the same sand after all of the mud balls and part of the coating were removed by running the sand through a hydraulic injector. The settlement was reduced, but it was still substantial. The lower line represents the settlement in a filter bed kept clean by a surface wash. The measurements on the surface-washed filter show that if the sand grains are kept reasonably free from coating there is little compacting of the bed while the filter is in service.

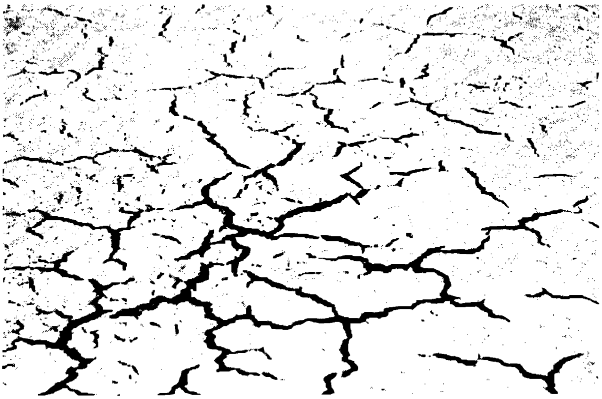


Fig. 21 Cracks in filter beds.

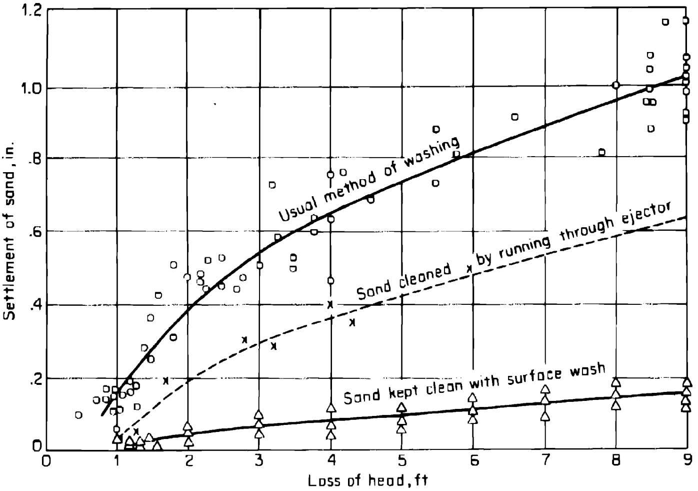


Fig. 22 Relation between the loss of head and settlement of sand in filters.

Pulling Away from Sidewalls

Settlement of the beds contributes to certain other filter bed troubles, for it allows beds to pull away from the sidewalls and at times permits cracks to open as shown in Figs. 23 and 24. Filter beds pull away from the sidewalls only when there is substantial contraction or settlement of the bed. Horizontal filtration begins to take place through the openings along the sidewalls, and it compresses the bed laterally. If the sand grains are so clean that the vertical compressibility of the bed is small, the bed cannot be compressed laterally. Cracks perhaps ⅛ in. wide may occur at the surface, and 2 to 4 in. below the surface with fairly clean sand, but no sidewall cracks will form.

Years ago, many filter beds pulled away from the sidewalls. At the ends of filter runs, some of them had pulled away from the sidewall as much as 1 in. at the top of the bed. By probing with a thin steel sheet down along the sidewall or by digging the sand away and observing the depth to which there was side filtration, as shown by the formation of a layer of mud near the wall similar to that at the surface, it was found that some of the sidewall cracks extended downward three quarters of the depth of 24-in. sand beds.

In plants where the sand accumulates a substantial coating, sidewall cracking cannot be prevented by backwash alone, even at the rates above 15 gpm/sq ft. Supplemental agitation appears to be the only means of keeping filter beds clean enough.

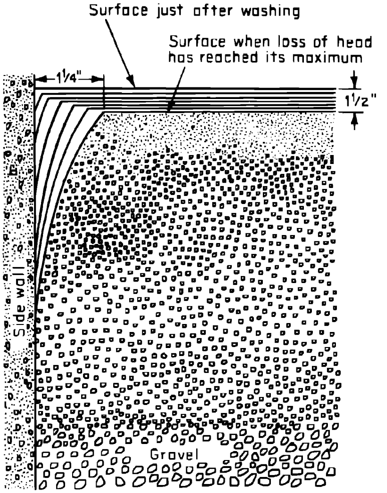

Surface just after washing
Surface when loss of head has reached its maximum
1¼"
1½"
Side wall
Gravel

Fig. 23 Cracks along sidewalls of filters.

Cracks along the sidewalls of filters are objectionable because: (1) finer media at the top of the bed, which is the most effective part of the bed, are bypassed; and (2) clogged areas are caused to form along the sidewalls.

Clogged Areas

For the formation of clogged areas there must first be an accumulation of mud or mud balls in the filter. This is succeeded by shrinkage of the bed as the loss of head increases.

There is a tendency for the mud balls near the surface of a filter to clump together during the washing process, especially where the expansion of the bed is not more than 20 to 30 per cent. This is more pronounced near the sidewalls than in other parts of the bed. If a clump of mud balls that is drifting about in the filter during washing moves over to the sidewall, it frequently remains there and grows by accretion until it becomes a clogged

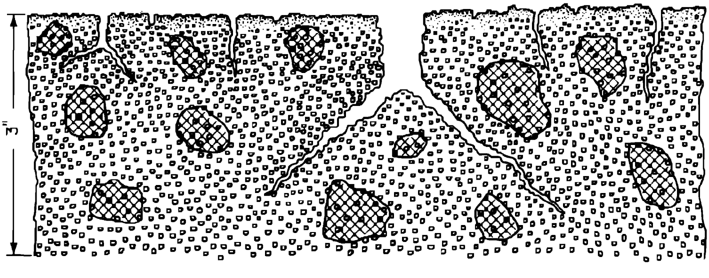


Fig. 24 Sketch showing typical surface cracks in top 3 in. of filter beds.

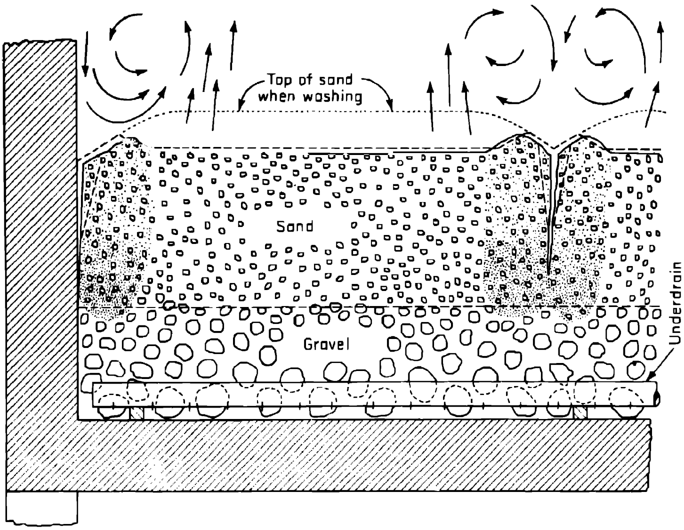


Fig. 25 Clogged areas in a filter bed.

mass as shown in Fig. 25. Additional clogged masses can form in other parts of the bed, as indicated in Fig. 25. The formation sometimes ends up with a filter looking like that shown in Fig. 26.

Figure 25 is a sketch illustrating both typical sidewall clogging and clogging in another part of the bed. The sidewall-clogged mass rests upon the gravel and does not adhere to the filter sidewall. It leans away from the sidewall as the loss of head increases, sometimes opening a crack all the way to the gravel. There is some side filtration through the clogged mass, especially in the upper part where the sand usually is not badly clogged, even though the mass is not agitated much during the washing because of the impermeable mass beneath it. There may be a very gradual displacement of this sand. The clogged mass moves against the sidewall during the washing period and is pushed away as the loss of head increases on the filter. In this condition the filter fails to do a satisfactory straining job.

Jet action helps pile up the mud balls at the gravel surface. Such pileups in turn accentuate the jet action. Prevention of mud ball formation by use of a surface wash at the top of the sand bed precludes the accumulation of mud balls at the gravel surface and thereby reduces the tendency of jet action to disrupt the filter bed.

The accumulated sediment which can be observed in the clear water reservoirs of many filtration plants is proof that suspended matter is getting past the filters. This is often due to shrinkage which leads to cracks along the sidewalls of the filters or cracks within the bed and to clogged masses in the beds. In some instances, such a condition constitutes a menace to health. In any event, the passage of any coagulated matter through the filter bed is objectionable and should be avoided even at considerable cost.

Pressure Sand Filters

Pressure filters are based on the same principle as gravity-type rapid-sand filters, but the underdrains, gravel, and sand are placed in a cylindrical tank, and the water is passed through the filter under pressure. In pressure filters the tank axis may be either vertical or horizontal. Filters of this type are intended for use where raw water is supplied under pressure and where it is desired to filter and deliver the water without further pumping. A cross section of a pressure filter is shown in Fig. 27.

Finished water from a pressure filter requires as careful pretreatment and as good a quality of applied water as would be necessary for finished water from free-surface filters. The extent and character of pretreatment are, of course, governed by the quality of the effluent desired.

Pressure filters are subject to the same operating difficulties as afflict standard rapid filters, except that air binding rarely occurs. Most of the troubles encountered are a result of careless operation or improper application of the water by the operator, both inherent in the nature of these filters. Their use for the production of a domestic water supply is not approved by some authorities.

Filters in Softening Plants

The conventional rapid-sand filter can be used for the clarification of lime-softened water as well as coagulated water, and the design details of filters for both services are substantially the same. In softening plants the

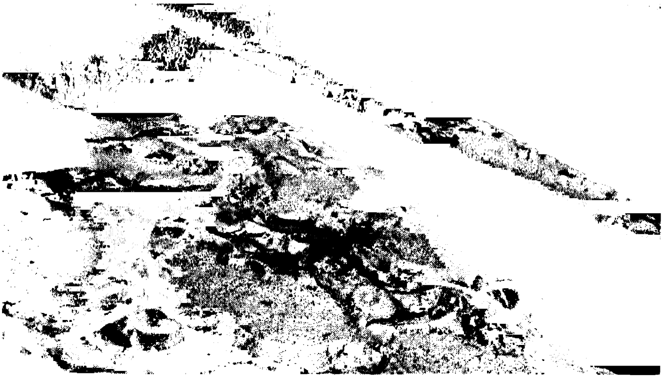


Fig. 26 Sand ridged by clogged places in the filter bed.

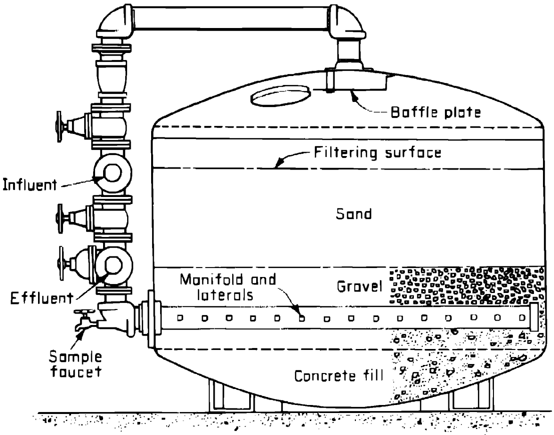


Fig. 27 Cross section of typical pressure filter.

function of the filter is to remove fine particles of calcium carbonate which have not been removed by the settling basin. The load on filters can be much heavier in softening plants, and more frequent backwash is sometimes needed. On the other hand, in some plants the precipitates produced are very dense and settle rapidly, and very long filter runs result.

There is a tendency for calcium carbonate to precipitate on the sand grains and to increase their size. In time, this process may increase the grain size to a point where backwashing is no longer effective, and the sand must be replaced. Recarbonation of the water ahead of the filters is frequently employed to prevent this difficulty. Some operators feed polyphosphate to the settled water to prevent this incrustation.

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7b

Diatomite Filtration of Potable Water

By E. ROBERT BAUMANN

INTRODUCTION

If water containing suspended solids is passed through a layer of porous media, some of the suspended and colloidal solids are removed, and the chemical characteristics of the water may be changed. This process is called "filtration," and its efficiency and cost are a function of:

1. The characteristics and concentration of the solids in suspension and the ions in solution
2. The characteristics of the filter media through which the water is passed
3. The method of filter operation

In general, a filter is usually referred to in terms of the type of filter media used and the quantitative rate of filtration, i.e., slow-sand filter, rapid-sand filter, high-rate rapid-sand filter, or diatomite filter.

The use of diatomite as a filter medium for filtration of potable water began during World War II when lightweight, portable equipment was needed to remove amoebic dysentery cysts from water.[1] Following the war, the initial civilian applications were for the filtration of water for swimming pools.[2,3] However, in 1957 diatomite filters had been used in

29 municipal installations, some of which had to be abandoned since they were designed, constructed, and operated on the basis of inadequate design and process information.[4] Since that time, more adequate knowledge of process and design requirements becomes available yearly. By 1964, some 81 diatomite filtration plants had been completed for the filtration of potable water, and over 60 per cent of new public swimming pools made use of these filters.[5]

DIATOMITE FILTER CHARACTERISTICS

Many diatomite filter plants can be designed to provide the desired quality of filtered water at a reasonable cost. The engineer should strive, however, to design the single plant which will provide that quality of water at the least cost commensurate with adequate standards of safety and reliability. Since the cost of filtration is a function of the first cost of the plant and the cost of labor, power, and filter media, the final filter design must be approached on a scientific basis.[6,7]

The design of a plant involves three major factors affecting filter operations:

1. The type and concentration of diatomite used as filter medium
2. The filtration rate
3. The pressure drop across the filter in feet of water

In general, water will be filtered at a constant rate of from 0.5 to 2.0 gpm/sq ft through a thin layer ($\frac{1}{8}$ in.) of filter medium which is applied as a "precoat" (at a rate of 0.1 to 0.15 lb/sq ft) to a porous "septum" which supports the filter medium throughout a filter run. During filtration, additional diatomite filter medium must be added continuously as a "body feed" to the unfiltered water. Body feed concentrations used should be adjusted in proportion to changes in the suspended solids in the raw water to maintain a filter cake of uniform permeability (Fig. 1). To obtain the minimum filtration cost, the flow rate, terminal head loss, and body feed rate will normally be such as to produce a filter run of over 24 hr duration.

Filter Media

The filter medium used in diatomite filters is manufactured from diatomaceous earth deposits which consist of the siliceous fossil remains of dead diatoms. The deposits differ in basic diatom structure from those of marine and freshwater origin. Nevertheless, satisfactory filter media can be made from these raw materials by adapting the production processes to the crudes available. The processed materials have unique structural properties which make them particularly suited for use as filter media in water filtration. This ~~structure~~ permits the formation of a rigid, porous, (90 per cent) retentive filter cake. The inherent clarifying ability, or "clarity in-

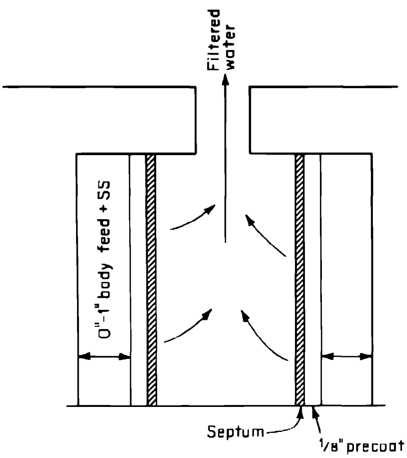

Fig. 1 Diatomite filter.

dex," of the processed diatomites is their most important property and is usually inversely proportional to their flow rate, or "permeability." Thus, as the relative permeability of the diatomites increases to allow more throughput, their clarifying ability decreases, i.e., they will pass larger suspended solids in the filtrate. Since different manufacturers are producing diatomite filter media from different crudes, their products may be comparable from a clarity standpoint and yet have substantially differing permeability, particle size distribution, color, wet or dry bulk density, and amount of oversize material. (The manufacturers of diatomite filter media have adopted and use the term "diatomite filter aids" for this material. To avoid confusion and to conform to the water industry's nomenclature, the terms "diatomite filter aids" and "filter aids" have not been used.)

Commercial diatomite filter media come in a variety of grades which are primarily based on relationships between clarifying ability and permeability (Table 7-2 and Fig. 2). Before an engineer can design a filter plant to produce acceptable water at least cost, he must select the proper filter medium for that particular water. The filter medium selected for use must provide a filtered water of satisfactory suspended-solids quality, yet simultaneously provide filter cake hydraulic characteristics which will result in economical operation. The proper choice would be to use the filter medium with the maximum permeability that will still provide desired clarity. At present, there is no standard specification for filter media accepted by the manufacturers or the waterworks industry. Table 7-2 and Fig. 2 show particle-size distributions and permeability data collected on a standard basis for typical commercial filter media.[8] No clarity index data are yet published, although most manufacturers use a sugar filtration test to evaluate the clarity index of their products. In general, the particle size, permeability, and clarifying index of any given grade of filter medium can be expected to vary from day to day as the crude and production processes change.

TABLE 7-2 Typical Values of K_3 for Various Commercial Grades of Filter Media[8]

Product	Mean particle size, microns	Approximate K_3, $\frac{\text{min/ft}^5}{\text{lb/gal}}$
Johns-Manville		
Celite 560	50	0.24
Celite 545	21.0	0.73
Celite 535	16.2	1.00
Celite 503	12.8	2.08
Hyflo Super-Cel	9.5	3.57
Great Lakes Carbon		
Dicalite 5000	21.8	0.68
Dicalite 4200	19.3	0.84
Speedex	13.0	2.55
Speedplus	10.4	3.83
Eagle-Picher		
FW-60	32.0	0.46
FW-50	19.3	0.97
FW-20	17.0	1.39
FW-14	12.0	2.96

In filter plant design, therefore, pilot plant tests should be conducted to determine the filter medium grade or grades which will provide the desired clarity-permeability relationship for that service. After a filter medium has been selected, it can be specified in a bid item as "grade X or equal." It will not, as yet, be practical to write one specification for a grade of a given flow rate or particle size that is applicable to all manufacturers. Diatomite filter media must be accepted or rejected on the basis of whether they conform to the clarity–flow rate characteristics of the medium that was used as the standard. Control limits and tests are still needed for making these decisions. Limits and tests can be adopted by individual users, but should be mutually acceptable to the filter media users and the manufacturers.

Diatomite Filter Apparatus

Diatomite filtration of water may be accomplished using either pressure or vacuum diatomite filters (Fig. 3). In the pressure filter, the filter septum and its layer of filter media are located in a pressure filter housing on the discharge side of the filter pump. Accordingly, the filter cake is always maintained at a pressure greater than atmospheric. The total pressure

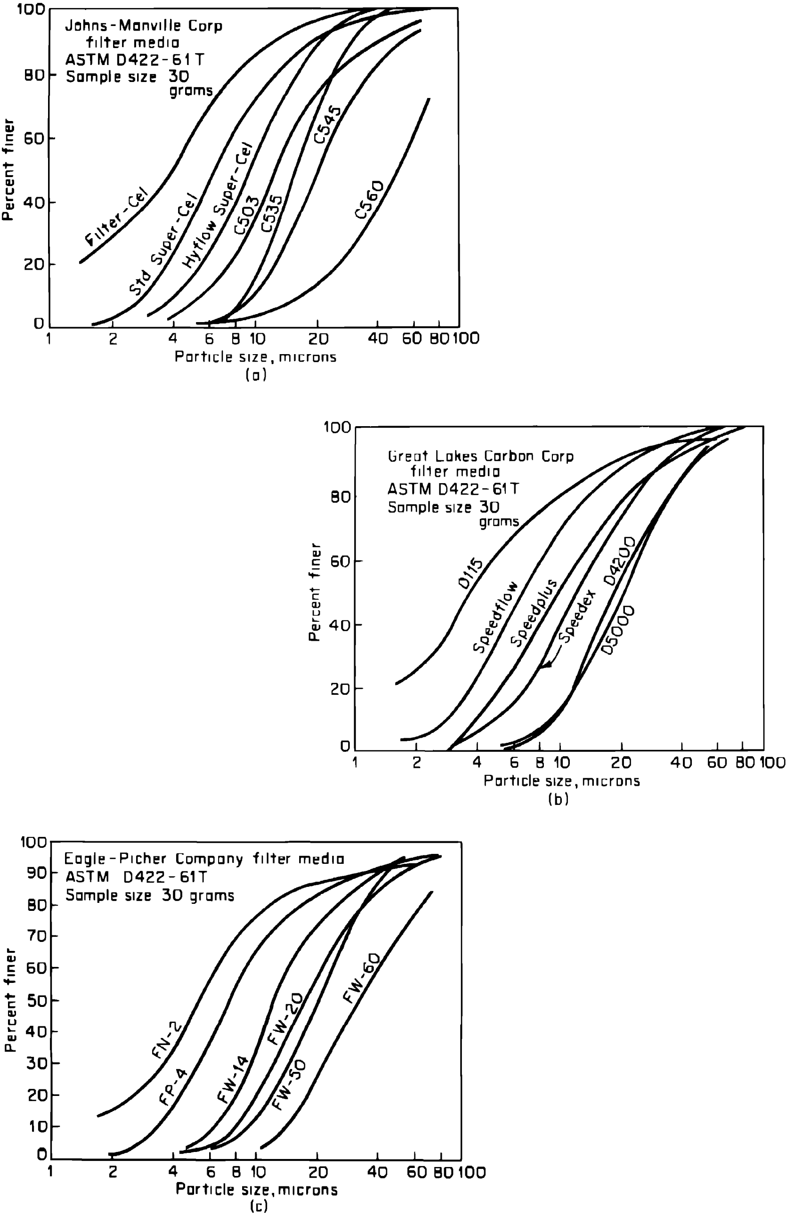

Fig. 2 Series II particle-size distributions for commercial filter-aid grades supplied by (*a*) Johns-Manville Corp.; (*b*) Great Lakes Carbon Corp.; and (*c*) Eagle-Picher Co.

drop or terminal head loss permitted across the filter is unlimited, since the pressure drop available will be determined by the hydraulic characteristics of the service pump. In practice, terminal pressure drops of 50 to 200 ft of water are used successfully.

In the vacuum filter, the filter septum and its layer of filter media are located in a filter housing open to the atmosphere on the suction side of the filter pump. As a result, the total pressure drop through the filter cake is limited to the total positive head of water above the filter plus the normal suction lift of the service pump. Although the theoretical suction lift of a pump is about 34 ft of water, the practical usable suction lift is only about 20 ft. Under these conditions, the practical terminal head loss in a vacuum filter is only 20 to 24 ft of water, and the filter cake will normally be at a pressure less than atmospheric (under negative head), except early in the run.

Both filters give identical results when operated at the same flow to the same terminal head loss. If dissolved gases (CO_2, O_2) are present in the water to be filtered, these gases will come out of solution in the filter cake which is under negative head in the vacuum filter. If the gas bubbles remain intact in the filter, they will serve to block the filter area and increase the cake thickness, resulting in a more rapid buildup of pressure drop. On the other hand, if the gas bubbles collapse, they may disrupt the uniformity

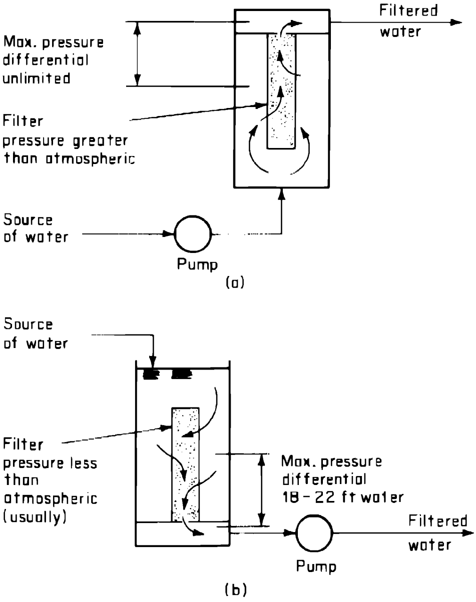
Max. pressure differential unlimited
Filter pressure greater than atmospheric
Filtered water
Source of water
Pump
(a)
Source of water
Filter pressure less than atmospheric (usually)
Max. pressure differential 18 - 22 ft water
Filtered water
Pump
(b)

Fig. 3 (*a*) Pressure filters; (*b*) vacuum filter.

of the filter cake and allow unfiltered water to pass through the cracks or openings formed and will serve to decrease the rate of head-loss buildup. Under such conditions, results differing from pressure filtration practice may be expected.

The pressure filter theoretically is more useful than the vacuum filter, since it can be designed to operate at any terminal pressure drop. Practically, however, the pressure housing inherent to the system makes it difficult to observe the effectiveness of the various filter operations and increases the cost of maintenance in repairing or replacing filter elements. The vacuum filter, though limited to 20 to 24 ft of terminal pressure drop across the filter, is much easier to operate and maintain. Vacuum filters will normally be used with clearer waters (swimming pool waters), while pressure filters will normally be used with more turbid waters.

Any diatomite filter installation should include all items considered essential for its proper operation. These items should be provided based on the knowledge that the operation of the plant must be simple, effective, safe, and dependable. The following items must be included in any satisfactory municipal installation:

1. *Service Pumps.* In municipal service, the installation should provide not less than two service pumps, one to provide service capacity and one for standby. Where water storage is less than half a day's usage, standby power should be provided.

2. *Rate-of-flow Indication and Control.* Each filter should be provided with equipment to indicate and maintain a constant rate of flow through the filters.

3. *Number of Filters.* Any installation designed to produce potable water should provide for not less than two filters.

4. *Body Feed Apparatus.* For proper operation, each installation must be provided with a body feed apparatus with an adjustable feed range adequate to fully cover the expected range of variation in the suspended solids in the raw water. Dry or slurry feeders can be used and preferably should deliver the body feed to the discharge side of the filter service pumps. Since diatomite filter media are dusty, and individual particles are fragile, dust-free handling equipment should be provided, and feeders should be designed to reduce or prevent the degradation of particles during feedings. Slow-speed mixers only should be used in slurry mix tanks. Body feed line flow velocities should be such as to prevent sedimentation of diatomite in the line.

5. *Filter Velocity Control.* To operate properly, both precoat and body feed filter media must be carried at the operating flow rate so that it will be deposited uniformly over the entire filter area. In other words, the mean cake thickness should not vary by more than plus or minus 10 per

cent of the mean thickness as determined by at least fifteen measurements made randomly and uniformly over the septum area. The installation should include a recirculation system to maintain adequate velocities in the filter system to prevent the filter medium from settling out before it is deposited uniformly on the septums.

6. *Filter Cake Control.* Where the possibility of interrupted operation of the filter cycle exists, the filter cake must not be allowed to slip or fall off the septums. Each installation should provide positive filter cake control during such periods. With all except horizontal, downward flow filters, a pump recirculation system should be provided to circulate water from the filtered water side of the septums to the raw water side at a flow rate sufficient to keep the filter cake in place. This system should automatically start when filtering is interrupted.

7. *Septums.* The septums to support the filter media must be rigid and structurally stable so that increasing pressure differentials resulting from filter cake buildup will not distort the septum and cause the filter cake to crack or be dislodged. The septum design should be such as to facilitate uniform precoating and rapid and effective cleaning. The septum assembly should be fixed so that a single septum can be quickly withdrawn, cleaned and/or repaired, and replaced.

8. *Storage.* As with any system, filtered water storage should be provided with diatomite filters. Waters which are normally biologically safe without treatment can be discharged after filtration directly into the distribution system. However, some storage should then be floated on the line. With marginally or moderately polluted raw waters, clear well storage must be provided. The storage vessel, whether clear well or elevated tank, should be provided with automatic controls to put the filter, body feeder, and velocity control recirculation system on a standby basis when the storage capacity is filled. A continuous flow to hold the filter cake in position must be maintained at all times during the filtration cycle. The automatic controls should return the filter system to production when the storage level falls.

9. *Disinfection.* All waters which are filtered through diatomite should be disinfected to meet the requirements of the appropriate reviewing authority.

Filter Operations

The proper functioning of a diatomite filter requires three separate and distinct operations: precoating, filtering, and septum cleaning. "Precoating" refers to operation of the filter during the period at the start of a filter run while the thin layer of precoat diatomite filter medium is being formed on the septum. The precoat filter medium should be added to the filter influent line so that it will be distributed uniformly in the flow. Only filtered water should be used during precoating. Water containing the precoat filter media should be filtered at a flow rate sufficient to keep the filter medium in suspension and to form a uniform precoat. The discharge from the filter should be circulated back to the influent side of the filter or should be run to waste. No water should flow during this period to the clear well or the distribution system.

Once the filter has been precoated (3 to 5 min), the service pump can then be used to deliver raw water to the filter, and the filter effluent can be diverted to the clear well or distribution system. During such "filtering cycles," body feed must be fed continuously to the raw water to provide a uniform permeability of filter cake. The body feed will also serve to fill any cracks which may momentarily form in the precoat as the pressure drop across the filter cake increases. No diatomite filter should ever be operated in the production of potable water without the continuous use of body feed. At the start of the filtering operation, the head loss across the filter septum and filter precoat will be about 0.5 to 1.5 ft of water, depending on the rate of flow, type of septum, and its degree of cleanliness. The rate-of-flow control will maintain a constant rate of flow through the filter by automatically adjusting so that the total pressure drop through the filter piping, filter cake, and controller will always be equal to the total pressure delivered by the pump at that flow rate. At the start of the run, most of the pressure drop will be in the controller, and it will be nearly closed. As the filter cake builds up and the filter cake head loss increases, the controller will open to reduce the loss through it by the same amount. When the controller is no longer able to adjust further, the filter rate will start to decrease, and the run should be terminated.

Once the filter run has been terminated, the "cleaning cycle" should begin immediately to wash the accumulated filter cake (precoat plus body feed plus suspended solids) from the filter housing. During such cleaning operations, only filtered water should be used. This water may be drawn from the filtered water side of the filter as in the air-bump backwash or may be supplied by a separate system. No direct connection should exist between the potable water supply and the filter cleaning system. Many types of pressure filter cleaning methods are used successfully—air-bump, reverse-flow, jetting, and air-gurgle. Where the filter area is readily available for maintenance, as in the vacuum filter, the use of high-velocity sluicing away of the filter cake with clear water will ordinarily be satisfactory. All cleaning methods should be designed to ensure adequate distribution of water to all parts of the filter area to free the filter area of filter cake and to dislodge the cake so it will be flushed completely out of the filter housing. No spent filter cake should be discharged to a sanitary or storm sewer system. A separate lagoon or filter should be provided for spent filter cake dewatering. Ultimate filter cake disposal should be to a sanitary landfill.

Potential Applications of Diatomite Filters

The diatomite filter is an acceptable tool in the waterworks industry, but is only a step in the water-treatment process, the details of which must be predicated on the characteristics of the raw water and what must be done to condition the water prior to filtration. Present municipal experience relates principally to turbidity removal from surface waters, but experience is growing with installations designed for iron and manganese removal from groundwaters and with filtration of lime–soda ash-softened water and coagulated surface waters. Municipal experience with turbidity removal has been principally where the actual turbidity is relatively low and the bacteriological quality is good, thus little pretreatment is provided. There is no common agreement on the upper limits of turbidity that can be handled without pretreatment. There has been some extension of the use of diatomite filters in some of the areas (i.e., marginally, moderately, and grossly polluted surface waters) which have been of particular concern to regulatory public health personnel. No one should recommend diatomite filtration in the near future for filtration of a grossly or even moderately polluted supply. However, appropriate prior conditioning of such waters by one of several available means, including coagulation and settling or chemical treatment of the filter medium or water to improve water filtrability, will undoubtedly lead to wider application of diatomite filters. Currently, effective water conditioning coupled with filtration through carefully engineered filters, an appropriate filter aid body feed system, and with adequate disinfection should provide a substantial margin of safety for marginally polluted waters and even sometimes for moderately polluted waters.

An advantage of a diatomite filtration plant for potable water is the lower first cost of such a plant. On waters containing low suspended solids, the diatomite filter installation cost should be somewhat lower than the cost of a conventional rapid-sand filtration plant. Diatomite filters will thus find application in potable water treatment under the following conditions:

1. In cases where the diatomite plant will be found to produce water at a lower total cost than any practical alternative.

2. In cases where financial capacity is tightly circumscribed, the lower first cost of a diatomite filter installation may be the major factor in the final choice of plant.

3. For emergency or standby service at locations experiencing large seasonal variations in water demand, the lower first cost of the diatomite filter may prove to be more economical.

THEORETICAL ASPECTS OF DIATOMITE FILTRATION

To obtain the maximum economy in the design and operation of a diatomite filter, an engineer will need to understand the probable effect of flow rate, terminal head loss, and body feed rate on the operation of the filter. The most important of these design items affecting filter operation is the prudent use of body feed during a filter run.

Effect of Concentration of Body Feed

The results of a typical series of filter runs conducted at a constant rate of filtration and to a constant terminal pressure drop, but with varying amounts of body feed, are shown in Fig. 4. The total volume of filtrate is plotted against the total head loss in feet of water. With no body feed or insufficient amounts of body feed, the head loss will increase more rapidly as the run continues, since the suspended solids are removed on the surface of the precoat filter medium and soon form a compressible, impermeable layer of solids which will not readily permit the passage of water. Under these conditions, the use of higher filtration rates would carry the suspended solids deeper into the precoat and more water could be filtered before the impermeable surface layer is completed. Thus more water might be filtered per run with higher filtration rates.

With further increases in the body feed, a filter medium concentration will be reached where the added diatomite will result in an increased porosity in the filter cake. This will serve to prevent the formation of an impermeable surface layer, and the rate of head loss buildup will be delayed. With large enough body feed rates the amount of filter medium in the cake may predominate and the resulting filter cake hydraulic characteristics may be more similar to those of the filter medium than those of the suspended solids removed in the filter cake. In this case, there will be a straight line rate of head loss increase with volume of filtrate. With still higher rates of body feed, the slope of the straight line plot will get flatter and flatter. Eventually, however, still higher rates of body feed will add

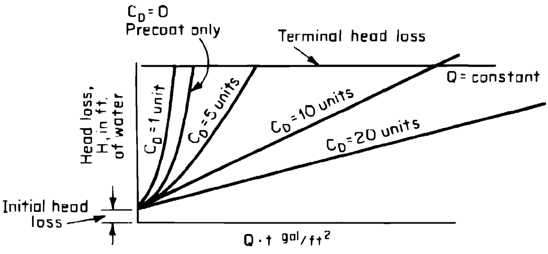

Fig. 4 Effect of varying the concentration of body feed C_D on the relationship of head loss to column of filtrate.

so much filter medium unnecessarily that the slope of the relationship of head loss to filtrate volume will again increase.

When the concentration of body feed is sufficient to produce a straight line relationship of head loss to volume of filtrate, the head loss through a given filter cake will vary directly with the flow rate. If the flow rate is then halved, the head loss through the cake will be halved. In fact, the ratio of the volume of water filtered at the lower filtration rate to the volume of water filtered at the higher filtration rate, Q_1t_1/Q_2t_2, will vary directly with the ratio of the higher unit flow rate to the lower filtration rate, Q_2/Q_1. In other words:

$$\frac{Q_1t_1}{Q_2t_2} \simeq \frac{Q_2}{Q_1}$$

Under these conditions, the volume of water filtered to any terminal head loss would be doubled by cutting the flow rate in half. If the volume of filtrate is doubled when the flow rate is cut in half, the filter run would need to last four times as long to produce that volume of filtrate. In fact, the ratio of the length of run at the lower filtration rate to the length of run at the higher filtration rate, t_1/t_2, will vary directly with the square of the ratio of the higher filtration rate to the lower filtration rate, Q_2/Q_1. For example,

$$\frac{Q_1 \cdot t_1}{Q_2 \cdot t_2} \simeq \frac{Q_2}{Q_1}$$

$$\frac{t_1}{t_2} \simeq \left(\frac{Q_2}{Q_1}\right)^2$$

When the rate of body feed used is sufficient to produce a straight line relationship between head loss and volume of filtrate, the hydraulic characteristics of the cake will be such that:[7]

1. The length of a filter run may be increased directly with an increase in the terminal head loss permitted across the filter cake at the end of the filter run.

2. The length of a filter run may be increased also by cutting the flow rate; for example, cutting the flow rate in half will increase the length of run by a factor of four times.

3. The volume of filtrate produced per unit weight of precoat used may be increased either by increasing the terminal head loss or by reducing the filtration rate.

If the terminal head loss is doubled or the flow rate cut in half, the volume of filtrate per run will be doubled and will increase the economy of diatomite use, since the same weight of precoat filter medium will produce twice the volume of filtrate.

In practice, the run length will normally have to exceed 24 hr in order to minimize labor costs involved in filter operation. The task of the engineer is to find the optimum combination of filtration rate, terminal pressure drop, and body feed concentration that will produce the filtered water at least cost.

Theory of Diatomite Filtration[9–11,13]

To minimize filtration costs, the engineer will first need to complete a number of pilot plant filtration tests to determine the hydraulic characteristics of filter cakes that result when body feed rates are sufficient to produce a straight line head loss to volume of filtrate relationship. A theory of diatomite filtration has recently been proposed which reduces the number of pilot plant tests which have to be made. The total head loss in a filter, H, is equal to the head loss in the precoat layer, h_1, plus the head loss in the body feed layer, h_2 [Eq. (1)]. The head loss in the precoat layer is a function of the rate of flow, the weight of filter media used in the precoat, and an impermeability coefficient K_3 which is a characteristic of the precoat filter medium used. Approximate values of K_3 for several commercial filter media are shown in Table 7-2.[8] The head loss in the body feed layer is a function of the body feed concentration added to the raw water, the square of the filtration rate, the time of filtration, and an impermeability coefficient K_4 which is characteristic of the body feed plus suspended-solids layer. The method used for the determination of both K_3 and K_4 in practice has been described.[9] Typical results showing the variation in K_4 of filter cakes used in the filtration of iron-bearing waters are shown in Fig. 5. Since K_3 and K_4 are temperature dependent, both impermeability coefficients are expressed at a standard temperature of 20°C (68°F). A value of K_3 of 0.56 at a water temperature of 68°F would increase to 0.86 at 40°F and would decrease to 0.38 at 100°F.[10] The following diatomite filtration equation assumes a constant water temperature:

$$\begin{aligned}\text{Total head loss} &= \text{head loss in precoat layer} + \text{head loss in body feed layer}\\ H &= h_1 + h_2\\ &= K_3 Q W_1 + K_4 C_D Q^2 t \times \frac{8.33}{10^6}\end{aligned}$$

where H = total head loss across filter cake, ft of water
Q = rate of filtration, gpm/sq ft
W_1 = weight of precoat, lb/sq ft
K_3 = permeability characteristic of the precoat filter-medium layer, min·ft^5/lb·gal
C_D = concentration of diatomite in body feed, ppm
t = length of filter run, min
K_4 = permeability characteristic of the body feed plus suspended-solids layer, min·ft^5/lb·gal

In order to design a diatomite filtration plant, the engineer could use

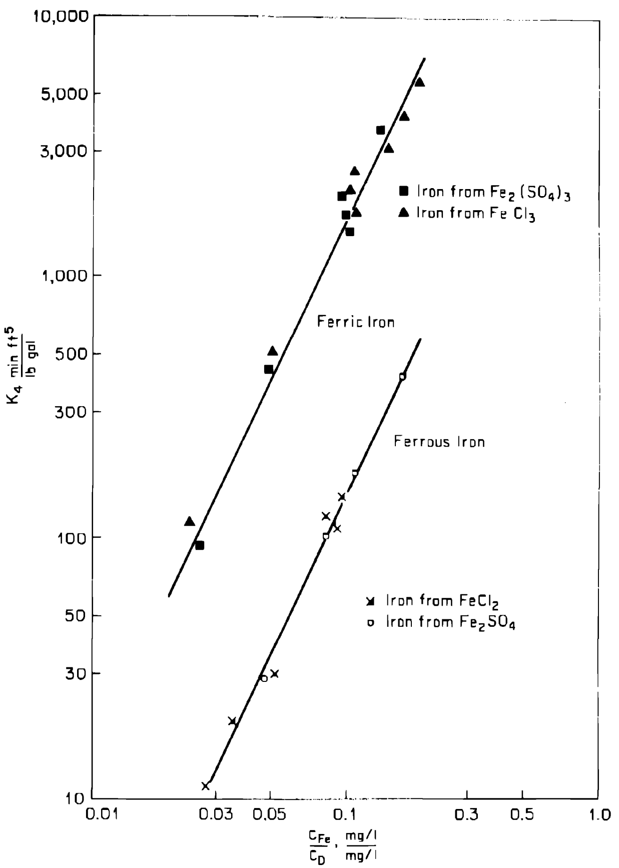

Fig. 5 Effect of source and type of iron on the relationship of K_4 to C_{Fe}/C_D.

Eq. (1) to predict the head loss, length of run, and volume of filtrate to be expected under any given set of operating conditions. He would then calculate filtration costs under the given conditions of operation. By checking all combinations of operating conditions, he can determine which combination will produce the least cost of filtration. To do this, he would need data concerning:

1. Costs of labor, power, and diatomite
2. Construction and maintenance costs of plants of various sizes
3. K_3 values of the filter medium used as precoat
4. K_4 values obtained when various concentrations of body feed are used to filter the raw water (Fig. 5)

More complete developments of the most recent theoretical equations used in diatomite filter design have been published[11] together with a description of techniques which can be used to determine filter cake resistance.[12] Practical examples of use of these theoretical developments in minimizing operating costs of new and existing plants have been described in detail.[13]

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8

Corrosion Phenomena–Causes and Cures

By T. E. LARSON

Corrosion is a phenomenon associated with a metal and its environment. For the purpose of this discussion, the environment will be water, generally of domestic quality. Corrosion takes place when a metal dissolves in water. In fact, some water must be present in almost all instances for metals to corrode, even if the chief environment is other than water. A second step in the process may be the deposition of the oxide of the metal at the corrosion site. Other metallic compounds such as carbonates or hydrated oxides may also deposit. These second-step products develop particularly when the water contains dissolved oxygen.

For a metal to corrode and thus to revert to its native stable state as an oxide is a natural tendency. However, due to differences in the mineral and gas contents of water supplies, some waters promote the solution of metal more rapidly than others. Others may help to develop a protective mineral or oxide layer against continued corrosion.

Waters which generally permit corrosion to take place are called "corrosive waters," and waters in which the metal does not corrode are called "noncorrosive" or "protective."

To add a degree of clarification and perhaps of confusion, different metals have different tendencies to corrode or not to corrode with the same water. One type of water may be corrosive to one metal and not another, but for a water of another quality, the reverse might be true. It is therefore difficult to make generalizations which are always true and, in fact, every generalization has its exceptions.

Physical factors which affect corrosion and corrosion control are temperature, velocity of water movement over the metal, changes in direction and velocity of flow, and contact with a second metal or nonmetal. At the risk of overgeneralization, several conditions usually hold true: Higher temperatures cause higher corrosion rates; higher velocities generally increase corrosion rates; wet contact with a second metal intensifies corrosion of one or the other. Notable exceptions and reversals of these generalizations will be pointed out later in this discussion. All are intimately associated with the mineral and gas composition of the water.

It is generally accepted that corrosion results from the flow of electric current between electrodes (anodic and cathodic areas) on the metal surface. These areas may be microscopic and in very close proximity, therefore causing general uniform corrosion and often "red water," or they may be large and somewhat remote from one another, causing pitting, with or without tuberculation. Electrode areas may be induced by various conditions, some due to the characteristics of the metal and some to the character of the water at the boundary surface. Especially significant are variations in the composition of the metal or the water from point to point on the contact surface. Impurities in the metal, sediment accumulations, adherent bacterial slimes, accumulations of the products of corrosion—all are related either directly or indirectly to the development of electrode areas for corrosion circuits.

In almost all forms of pipe corrosion, the metal goes into solution at the anode areas. Because a movement of electrons occurs on solution of the metal, the metal develops an electric potential. Electrons liberated at these areas flow through the metal to the cathode areas where they become involved in another chemical reaction, and the metal develops another electric potential. Control of corrosion by water treatment methods aims at retarding either or both of the primary electrode reactions.

Because electric currents are carried by ions as conductors in water, and because these ions affect the potentials at both the anode and cathode, some discussion of the soluble components in water is warranted.

Almost all mineral salts dissolve in water to some extent, from insignificant traces to gross concentrations exceeding that of salt in seawater. On solution, these salts separate into two types of ions, anions and cations, which have opposite electric charges and are kept apart by water itself. These ions are responsible for the ability of "water" to conduct an electric current. Pure water has relatively few ions. Only 0.0001 per cent of water separates into hydrogen cations and hydroxide anions. Therefore pure water, free from mineral salts, has very little capacity for carrying electric current. Its electric conductivity is extremely low.

However, when minerals are dissolved in water, the resultant ions provide the necessary conductivity to permit corrosion currents to flow, with negatively charged anions moving to the anode and positively charged cations moving to the cathode. Their accumulation at the respective electrodes is limited by other reactions which take place at these points.

The basic electrode reactions involving the transfer of electrons may be represented as follows:

Anode: $Fe - 2e \rightarrow Fe^{++}$

Cathode: $2e + 2H_2O \rightarrow H_2 + 2OH^-$

When dissolved oxygen is present, the cathode reaction may be represented as $2e + H_2O + \frac{1}{2}O_2 \rightarrow 2OH^-$. Therefore with or without dissolved oxygen the same amount of hydroxide ion is formed at the cathode, and an alkaline condition prevails.

The effect of dissolved oxygen is felt in a critical way at the anode where the following side reactions can take place:

$$2Fe^{++} + H_2O + \tfrac{1}{2}\ O_2 \rightarrow 2Fe^{+++} + 2OH^-$$

The ferrous (Fe^{++}) iron is oxidized to the ferric (Fe^{+++}) state and reacts with water (hydrolyzes) to precipitate the insoluble ferric hydroxide (iron rust):

$$Fe^{+++} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$$

The overall result is the formation of hydrogen ions which maintain a condition of acidity at this point:

$$2Fe^{++} + 5H_2O + \tfrac{1}{2}\ O_2 \rightarrow 2Fe(OH)_3 + 4H^+$$

The acidity at this point increases the solution rate of iron and maintains a high potential difference between the anode and cathode areas.

The corrosion rate is limited by the diffusion rate of dissolved oxygen to the anode corrosion product. The greater the dissolved oxygen concentration, the greater will be the rate of diffusion. Likewise, the greater the velocity of flows past the anode, the greater will be the rate at which dissolved oxygen is brought to the anode products. The net result of oxygen delivered to the anode area is to increase the corrosion rates. The diffusion to the anode itself is limited somewhat by the physical barrier of porous ferric hydroxide over the anode surface.

At the cathode, dissolved oxygen affects the alkaline condition, because the ease of formation of hydroxide ions is greater in the presence of oxygen, therefore the OH^- concentration increases at a more rapid rate. The diffusion rate of dissolved oxygen is also affected here by the concentration and the velocity of flow of the water past the cathode. However, with high concentrations of calcium and bicarbonate as well as carbonate ions, the rate at which these are brought to the hydroxide ions at the cathode is also greater. The net reaction with the hydroxide ions is as follows:

$$Ca^{++} + HCO_3^- + OH^- \rightarrow CaCO_3$$

and the result is to provide a dense barrier that reduces the diffusion rate for dissolved oxygen to this area and correspondingly reduces the corrosion rate.

This brief summary does not include discussion of many other factors, such as relative conductivity of ions, relative potential of different metals, the effect of hydrogen or hydroxide ions on these potentials, polarization, and the diffusion of anions and cations. It is evident, however, that the primary and secondary reactions offer a highly complex set of mechanisms which are interrelated and dependent to a great extent on the mineral and gas content of the water.

Iron has been used as the example metal. With notable variations, similar mechanisms and reactions are involved with other metals. Because of these variations, all metals do not corrode equally with each water.

Steel has excellent structural properties and is used extensively where possible in the water industry. However, experience has usually dictated that protective measures be used when steel is exposed in a water environment. In some instances, severe chemical treatment is substituted for coatings when the water is not used for domestic purposes. Steel pipe and other steel containers are seldom used for water distribution systems or household or industrial water uses without protective coatings of zinc (galvanized iron), cement, enamel, paint, or heavy bitumastic or coal tar. Such coatings are necessary not only to reduce corrosion and the loss of structural strength but also to avoid rust and "red water" problems. Coatings, however, must be complete and continuous to be entirely effective.

Hazardous corrosion conditions can develop at holidays in the coatings, at joints, or other exposures of bare metal. The effect of water quality is noted at these points, and the results are of great concern. The degree of corrosion hazard is, to a considerable extent, dependent on the water quality.

The following classification of waters considers the mineral content, dissolved oxygen, and pH (acidity) relative to the effect on the corrosion of mild steel.[1]

GENERAL CLASSIFICATION BY WATER QUALITY

No Minerals—Dissolved Oxygen Present. In the absence of minerals, increasing pH decreases corrosion rates by water containing dissolved oxygen. However, if the pH is near, but not above, that required for complete protection, pitting occurs, which rapidly decreases the useful life of mild steel. Crevices at joints and welds which do not permit oxygen to be maintained at the surface are subject to localized corrosive attack.

Pitting takes place at local unprotected points of corrosion where the corrosion products prevent the diffusion of oxygen to the metal surface and thereby create differences in oxygen concentration at the metal surface. Similar pitting can occur under deposits of debris. Also, differences in oxygen concentration as at the water line of surfaces exposed partly to air and partly to water will cause pitting. The rate of corrosion increases at higher temperatures.

No Minerals—Dissolved Oxygen Absent. In the absence of dissolved oxygen, the pH of "high-purity" water in mild steel containers adjusts itself to about 8.4 and corrosion becomes negligible. However, all natural waters are mineralized to some degree.

Noncarbonate Minerals—Dissolved Oxygen Present. In the absence of carbonate minerals increasing concentrations of other common minerals such as chloride and sulfate salts increase the corrosion rate at all pH values below the pitting range of pH and increase pitting when the pH is just below that required for protection in the presence of dissolved oxygen. Increasing temperature accelerates both general corrosion and pitting.

Carbonate Minerals (No Calcium)—Dissolved Oxygen Present. Carbonate minerals indicated by the alkalinity determination for bicarbonates inhibit corrosion, acting to counter the acceleration effect of salts of chloride and sulfate in waters containing dissolved oxygen. In the absence of calcium, this inhibition is maximum at a pH of 6.5 to 7.0 when the alkalinity concentration is more than five to ten times the chloride and sulfate salt concentration and is minimum at a pH of 8 to 9. At alkalinity concentrations below five or ten times the chloride and sulfate salts, corrosion rates increase. Nearly all natural domestic waters or carbonate minerals contain both alkalinity and chloride and sulfate salts.

Minerals—Dissolved Oxygen Absent. In the absence of dissolved oxygen, the types of mineralizations are less important with respect to useful life of mild steel as indicated by the following two examples: (1) Plumbing experience has indicated that properly designed hot-water heating systems can be made of steel provided no water (domestic) is lost from the system; avoiding the addition of make-up water containing dissolved oxygen also prevents loss of corrosion products that inhibit the corrosion; (2) the useful life of steel used for feedwater heaters, boilers, and piping for power plants may be extended considerably by maintaining an oxygen-free boiler feedwater.

Calcium Salts—Dissolved Oxygen Present. From the standpoint of corrosivity, stability as indicated by saturation with calcium carbonate is the most widely accepted criterion in classification. However, for uncoated mild steel, a very significant supersaturation must exist to form a visible deposit, and even this criterion is not infallible. It has specific limitations:

1. A minimum alkalinity of 50 to 100 ppm and a minimum of about 50 ppm calcium (calculated as $CaCO_3$) must be present at normal temperatures (32 to 160 °F) for even a small degree of protection.
2. The greater the concentrations of calcium and alkalinity, the greater is the capacity for protective action by the water. However, increasingly high concentrations are responsible for an increasing tendency to deposit objectionable quantities of scale at temperatures above that at which saturation stability is established.
3. The protective action is enhanced by movement of the water and decreased at near-stagnant conditions.
4. The protective action may be nullified at higher temperatures when the pH is high enough to deposit nonprotective magnesium hydroxide.
5. Pitting and tuberculation will occur in the presence of dissolved oxygen if the stability and velocity are near, but still below, that required for complete protection.
6. The protective action is decreased by increasing proportions of chloride and sulfate salts above a ratio of about 0.1 or 0.2:1 with respect to alkalinity. This limitation becomes less significant in the absence of dissolved oxygen.

TYPES OF CORROSION

There are many types of corrosion. Each has its own characteristics and offers clues to the causes and sometimes to the characteristics of the environment. Possible types of control may also be deduced.

Uniform corrosion is recognized as taking place at a generally equal rate over the surface. The loss in weight is directly proportional to the time of exposure, and the rate of corrosion is constant. It is usually associated with acids or with water having a very low pH and very few protective properties. Mild steel in neutral, low-calcium, and low-alkalinity salt water corrodes at a rather uniform rate.

Pitting corrosion is nonuniform and more generally observed than uniform corrosion. It occurs in an environment which offers some but not complete protection. The pit develops at a localized anodic point on the surface and continues by virtue of a large cathodic area surrounding the anode. Chloride ions are particularly notorious for their association with this type of corrosion of steel. Even stainless steel is subject to pitting corrosion with relatively high chloride solutions. Pits may be sharp and deep or shallow and broad, and can occur without chlorides. In water containing dissolved oxygen, the oxide corrosion products deposit over the site of the pitting action and form tubercules.

Pitting-type corrosion may also be associated with galvanic corrosion, concentration corrosion, and crevice corrosion.

Galvanic corrosion is associated with the contact of two different metals or alloys in the same environment. Almost all metals and substances have different solution potentials, whether in the same or in different environments. When two metals come together, the difference in potential results in current flow, and one of the metals becomes anodic to the other, which serves as the cathode. The anodic metal corrodes and the cathodic metal does not (or if so at a relatively low rate). *The cathodic metal is said to be protected at the expense of the anodic metal.* To be exact, all corrosion is galvanic in the sense that an electrochemical cell is the source of the corrosion current.

The rate of galvanic corrosion is increased by greater differences in potential between the two metals. It is increased by large areas of cathode relative to the area of the anode. It is generally increased by closeness of the two metals and also by increased mineralization or conductivity of the water.

Galvanic corrosion is often a great source of difficulty where brass, bronze, or copper is in direct contact with aluminum, galvanized iron, or iron. Copper-bearing metals are cathodic to aluminum, zinc, and iron, and their underwater contact very often results in corrosion of the latter metals. Similarly, mill scale on steel is cathodic to the steel; iron oxide is cathodic to iron; cement is cathodic to copper; carbon is cathodic to iron; iron is cathodic to aluminum and to zinc.

Galvanized (zinc-coated) steel is usually more serviceable than steel alone, because the iron exposed at joints and holidays is protected at the expense of the zinc. In general, longer life may be expected with greater thickness of the zinc coating. Zinc in many natural waters containing alkalinity of 50 to 100 mg/l or more will form an insoluble protective coating of zinc carbonate or zinc hydroxyl carbonate in the pH range of 7.5 to 8.5 at room temperature or lower. In hot-water tanks, there is some evidence that zinc becomes cathodic to iron at temperatures above 140 to 160°F with certain types of waters. Traces of copper (0.1 mg/l) in the water can "plate out" on zinc or iron and result in local pitting. Copper-containing waters have a similar, more serious, effect on aluminum.

Concentration-cell corrosion is perhaps the most prevalent type of corrosion, and because it is difficult to ascertain by field measurement, it is usually deduced by inference. It occurs when there are differences in the total or the type of mineralization of the environment. Differences in acidity (pH), metal-ion concentration, anion concentration, or dissolved oxygen cause differences in the solution potential of the same metal. Differences in temperature can also induce differences in the solution potential of the same metal.

It has previously been noted that in water containing dissolved oxygen, the corrosion products deposit at the anode, and in the secondary reaction of oxidation of ferrous iron to ferric iron and subsequent hydrolysis, hydrogen ions are formed. This greater acidity at the anode results in a hydrogen-ion concentration cell at this point, and increases the rate of corrosion. In the same instance, dissolved oxygen cannot diffuse or penetrate to the anode surface because it first reacts with the ferrous iron; thus there is an absence of oxygen at the anode. But oxygen can diffuse to the cathode area and result in an oxygen concentration cell which also increases the rate of corrosion at the point of absence of oxygen. Likewise, it has been previously noted that hydroxyl ions accumulate at the cathode area, resulting in drastic reduction in hydrogen-ion concentration, which therefore enhances the concentration cell related to the development of hydrogen ions at the anode.

It should be noted that although the dissolved oxygen usually stimulates corrosion, the loss in metal takes place at the anode, where there is no dissolved oxygen.

Oxygen concentration cells develop at water surfaces exposed to air, accelerating corrosion a short distance below the surface. The dissolved oxygen concentration is replaced by diffusion from air and remains high at and near the surface, but does not replenish as rapidly at lower depths because of the distance. Therefore the corrosion takes place at a level slightly *below* the surface rather than at the surface.

Dirt and debris or local chemical precipitates on a metal surface hinder oxygen diffusion by covering the metal at local areas. Thus, corrosion takes place under the deposit.

Thus it is evident that any nonadherent deposition on metal can start a chain of circumstances which result in an oxygen concentration cell.

Crevice corrosion might be classed as a form of concentration corrosion because when oxygen is spent on corrosion in a crevice, it is difficult for more oxygen to reach the metal by diffusion into the depths of the crevice. The crack or crevice or the uneven joint between two surfaces of the same metal bound together face to face behaves as a pit where oxygen can reach the exposed surface but becomes deficient in the crevice, thus forming an oxygen concentration cell whereby corrosion takes place in the crevice.

Dezincification is the result of removal of zinc from its alloy with copper (brass). Copper remains at the surface of the brass as the zinc is dissolved.

Soft unstable waters, especially those with a high CO_2 content, are particularly aggressive to Muntz metal and yellow brass. Red brass and Admiralty metal are more resistant. The occurrence of plug-type dezincification and dezincification at threaded joints suggests that debris and crevices may initiate oxygen concentration cells and result in dezincification.

Graphitization is a form of corrosion of cast iron in highly mineralized water or waters with a low pH, which results in the removal of the iron silicon metal alloy making up one of the phases of the cast iron microstructure. A black, spongy-appearing, but hard mass of graphite remains. The graphite dispersed in the cast iron serves as the cathode for a large number of small galvanic cells, and the iron-silicon alloy becomes the anode.

Cast-iron products derive their shape from the freezing of a liquid alloy in a mold; thus solidification takes place under different conditions over the cross section of any cast shape. The portion near the mold wall may have a different composition, freezing rate, and structure than the material farther from the mold wall. There is likely to be less graphite at the surface of the casting; thus the familiar observation that machining of cast iron produces a lower corrosion resistance at the machined areas.

The high corrosion resistance of cast iron in soil is probably due to the formation of a silicate film which together with the initial corrosion products forms an effective barrier. In mine water having a low pH and high concentrations of iron and/or copper salts, the silicate film may be quite soluble. The removal of the film then causes rapid corrosion of the metallic phases of the cast iron, leaving the skeleton of graphite embedded in corrosion products.

Stress corrosion results from tensile stress, usually of external origin, on the metal or alloy. The corrosion usually (but not always) takes place selectively at the microstructure grain boundaries in the metal. Repeated rupture of a protective film on the surface provides a continuously anodic region.

Corrosion fatigue resulting from alternate stress conditions is usually more rapid than steady-state stress corrosion. The alternation of the stress disturbs such protective film as may develop at the anode site and enhances the rate of corrosion.

Erosion corrosion results from the removal of the protective film of corrosion products, which serves as a barrier to corrosive attack of some metals. Many metals such as aluminum, austenitic stainless steel, and passive iron are completely protected by a film (such as aluminum oxide on aluminum in favorable environments). The erosion, generally at high velocity, may take place through removal of the film by abrasive, suspended material. Friction between two adjoining surfaces may also permit corrosion to continue.

Impingement attack on copper pipe is also an apparent example of erosion corrosion, as it is particularly evident at velocities greater than 5 to 8 fps and at sudden changes in direction of flow at joints and elbows.

Cavitation corrosion is usually associated with high velocity and sudden changes in velocity direction which causes gas-bubble formation and resolution of the gases. The attack occurs downstream from the direction change caused by a constriction such as a valve or protrusion at a joint. Carbon dioxide in the gas bubbles develops an acidic film at the water surface. If oxygen is present, its concentration at the water surface is also greater than in the body of the water and further accelerates corrosion.

Wire drawing in faucet seats appears as grooves across the face. This is an apparent type of cavitation corrosion or erosion corrosion in which chloramine serves as a corrosion accelerator. Monel metal seems to be the only alloy that resists this attack.

Stray currents have often been blamed for corrosion occurrences where other causes have been present. With direct-current electric railways, serious corrosion problems with underground structures have properly been traced to stray currents, but almost invariably this has been external corrosion of piping rather than internal. All metals have greater conductivity than the surrounding environment, and current will stay with the metal until there is a discontinuity. An excess of electrons will leave the metal at the points where the environment is more highly conductive and closest to another conductive receptor for the current. Corrosion takes place at the anode, the point where the current leaves the metal to be returned to the power source. Currents find and travel by the path of least resistance.

The use of insulating connections or proper countercurrent applications such as cathodic protection can eliminate this problem. However, improper use, without a satisfactory survey of the problem and advice by specialists, can result in accelerated corrosion rather than prevention.

Effect of Velocity

The corrosion problem as related to water velocity is of course manifested in two contradictory ways. For aggressive water, high velocities are of course conducive to rapid pipe deterioration but with little show of metal pickup in the water, whereas at low velocities with longer time of contact the pipe deterioration may be slow but significant metal concentration develops in the water (red water).

However, less aggressive waters with protective properties are more able to protect the surface at higher velocities. Therefore, with adequate inhibitor concentration, higher velocities normally not only prevent metal deterioration but also dissolve less metal per unit volume of water.

At low velocities, the protective properties of inhibited waters are not utilized to their best advantage, since the slow movement does not aid the effective diffusion rate of the protective ingredients to the metal surface. Therefore a water which behaves satisfactorily at medium-to-high velocities may still cause incipient or slow corrosion with accompanying red water problems at low velocities.

Effect of Temperature

The influence of temperature is also often confused by conflicting observations. This confusion can best be avoided by recognizing basic equilibria in water chemistry. Basically, higher temperatures cause more rapid chemical reaction rates and generally reduce the solubility of minerals. However, the effect of temperature on pH is seldom recognized. For pure water, pH decreases or the H^+ concentration increases (as does the OH^- concentration) with increasing temperature. But the *degree* of influence of temperature on pH is a function of the alkalinity of the water. Increasing concentrations of bicarbonate increasingly buffer or hinder this effect of temperature on pH. Further, it is commonly assumed that the solubility of $CaCO_3$ decreases with increase in temperature. This is not true for waters of low alkalinity (less than 50 ppm). In such waters, the greater temperatures decrease the pH at a rate which is greater than the rate of decrease in solubility of $CaCO_3$. This decrease in pH actually increases the *solubility* of $CaCO_3$ even though the *solubility product* of $CaCO_3$ decreases. This effect on the saturation index is particularly acute for 10 ppm alkalinity and even for 25 ppm alkalinity with a temperature change to 130 °F and more so to 160 °F.

If we consider hot-water heaters and storage tanks, this also explains, in part, the poor reputation shared by a great number of water supplies, since the alkalinity is too low to buffer the effect of temperature. In hot water tanks the problem is further aggravated by the low velocities which prevent almost any chemical protective measure from being effective.

Sulfate-reducing Bacteria

One other possible factor in corrosion is worthy of mention. This concerns the effect of sulfate-reducing bacteria. Corrosion induced by such bacteria is not uncommon on the soil side of pipe, but is seldom discussed in connection with internal pipe corrosion. This has been due to the former absence of a good test for the organisms and the assumption that the organism will not live in the presence of air or chlorine. This may well be true, but there are mounting data to show the presence of such bacteria in distribution systems. This results from new procedures for their cultivation in water samples.

Their presence may be explained by the fact that the underside of tubercules provides an anaerobic environment with an oxidation-reduction potential (ORP) probably less than —100, and neither chlorine nor dissolved oxygen can get to them. Their mode of growth is usually ascribed to a reaction of sulfate with organic matter or hydrogen as reducing agents to form H_2S. More recent information suggests that they do not thrive on hydrogen without organic matter, but hydrogen accelerates growth. There should possibly be further exploration to determine if the ferrous ion as a reducing agent accelerates growth. Oxidation and precipitation of magnetite (Fe_3O_4) as well as ferrous sulfide would result in an excess of hydrogen ions to enhance the corrosion rate of iron.

Too little is known about the significance of these organisms in corrosion by domestic waters.

Ammonium-oxidizing bacteria convert ammonia in the presence of oxygen to nitrite, which is further oxidized by oxygen to nitrate, thus converting a cation to an anion, which results in an increase of hydrogen ions. Again, too little is known about the magnitude of this effect, and proof is absent on the association of these bacteria with corrosion.

CORROSION CONTROL

If corrosion is not checked, costly replacement is inevitable. But long before this point is reached, the ill effects of corrosion are felt. The quality of the water deteriorates; carrying capacity decreases, with consequent rise in pumping costs; cooling with the water requires excessive water use, because heat transfer is retarded by deposits of corrosion products.

Protective measures against corrosion include: use of copper or copper alloy instead of galvanized iron in manufacture; coating with zinc (steel pipe) or coal tar (cast-iron pipe); lining with cement; and in-place coating after main cleaning.

Chemical control is a *supplement* to these measures, not a substitute for them. Moreover, chemical control cannot be expected to overcome improper flow conditions, poorly designed distribution systems, defective materials, grossly faulty coatings, and underdesign of copper pipe.

Chemical control involves expense and constant surveillance. The chemicals are costly and require proper feeders as well as storage. They must be carefully selected and can be hazardous to personnel if handled carelessly. Analytical tests must be made at regular intervals to ensure proper applications and to evaluate performance. None of these problems are insurmountable, however, and as more is learned about chemical control, its role should become increasingly important.

On the whole, chemical control has been more successful with water for industry than with water for drinking. In the industrial processes, chronic or acute toxicity is not generally a significant factor, and therefore there is no serious restriction in kind and quantity of chemical control. Because the water is not used for drinking or other environmental purposes, high concentrations of inhibitors, such as chromates, nitrates, phosphates, organics (such as tannin), and synthetics (such as mercaptans) can be tolerated and, when quantity requirements are low, are economical.

For example, chromates, phosphates, and organics have been used in relatively large quantities with exceptional success in treatment of cooling water cycled through heat exchangers and cooling towers. Preheaters with scavenger chemical treatment and pH adjustment are also effective and are economic assets to boiler feedwater control. With water for drinking, however, there are serious limitations on kind of chemicals used, because of effects on taste, odor, color, turbidity, and toxicity, and almost equally serious limitations on quantity, because a great volume of water must be supplied at low cost, and the water once used is not recycled.

Polyphosphate Treatment

The presence of iron in the water is not necessarily an indication of corrosion, because it may have been present in the water before contact with the metal vessel. The appearance of a rusty scale is not always evidence of corrosion, because it may be a deposition of hardness together with iron which was originally present in the water.

Polyphosphates have been reported to be effective in reducing corrosion by domestic waters. The reliable data show this effectiveness only under certain conditions with relatively high concentrations and with certain types of waters. Corrosion prevention cannot be claimed, even though the red-water effects of natural iron in the water have been lessened by the use of polyphosphates; nor can prevention be claimed where red water is avoided by sequestration of this iron corrosion product. Improvement but not prevention can be claimed in situations where pitting-type corrosion is altered to generalized corrosion.

The effectiveness of polyphosphates is progressively greater at increasing turbulent velocities and at increasing concentrations. Under essentially no conditions are polyphosphates effective in stagnant or nearly stagnant water, such as in deadends or service lines. The only data available on its effectiveness at low velocities appear to indicate slight increase in corrosion at 0.5 fps. It should be recognized that conditions of 2 to 5 fps or more of turbulent flow velocities are not experienced continually in all parts of almost any distribution system, and certainly not in communities where the grid has been designed with 5 to 10 miles of 4- and 6-in. pipe for a 30,000-gpd consumption.

In hot-water systems, the corrosion rates are usually greater than in cold, because the polyphosphates have a greater tendency to decompose and revert to phosphoric acid at higher temperatures. Recirculation improves the effectiveness of polyphosphates or of any inhibitor in hot-water *systems,* but, because of the low velocity, not in hot-water *tanks.* It can, however, improve the ability of the treatment to maintain in solution such iron as is dissolved by corrosion.

Silicate Treatment

A popular treatment for corrosion control, particularly on waters with very low hardness, alkalinity, and pH less than about 8.4, is the use of sodium silicate in one of the various proportions of Na_2O and SiO_2. Its effectiveness is apparently dependent on the adsorption of silica in the hydroxide corrosion products of iron and zinc. It is said that the dosage should be independent of the natural silica in the water, but no specific concentrations are recommended for the various conditions of water quality. Treatment must be relatively continuous, and effectiveness is favored by high velocity and generally lower pH levels.

PIPE CORROSION

Copper Service

Copper piping generally enjoys a good reputation when used with oxygen-free hard water, a prevalent characteristic of groundwater in many areas of the country. However, with dissolved oxygen in excess of 2 ppm and carbon dioxide in excess of 10 ppm with no hardness, above an upper limit of 140 °F and 4 fps *continuous* velocity, erosion corrosion often begins to become a significant problem.[2]

The presence of chloride and/or sulfate ions tends to increase the corrosiveness, particularly for soft waters of very low alkalinity that are unsaturated with respect to calcium carbonate. The conditions under which nitrate ions accelerate corrosion of copper have not been clearly defined.

These limits can be alleviated (1) by blending with hard water and/or increasing the pH to reach the saturation point for calcium carbonate or reducing the carbon dioxide to less than 5 ppm, (2) by cold deaeration to substantially reduce the dissolved oxygen and carbon dioxide content, or (3) by intermittent flow through the service line to permit the development of corrosion product films.[2]

Distribution Systems

By far the greatest mileage of present distribution systems consists of cast-iron pipe, and the following comments are therefore directed primarily to use of this material. These remarks must not be quoted out of context and can only be classed as generalizations. Organic coatings such as enamels or tar and bituminous coatings are effective only to the extent of their coverage and durability. The same can be said for the newer organics such as epoxy coatings. The tar and bitumastic coatings have in many installations, particularly for unaerated groundwater, performed a yeoman service, but have on occasion failed when used for unstabilized soft surface waters and for some aerated groundwaters. Many of these failures could have been prevented by adequate water treatment.

The best general records of success with coatings appear to center about cement linings, and usually these records are dependent on the quality of the water. With hard waters the record is very good, but with soft waters the record is less enviable. However, for many years now, cement linings have met with good to excellent success.

What is said about cement linings is generally equally applicable to cement-lined steel and to nonmetallic pipes such as asbestos cement. Other nonmetallic pipes such as plastic have yet to be made competitive.

The remaining prevention-and-cure methods lie in alteration of the environment and in hydraulic design. These two factors are associated because the design as related to the velocity of flow can be a strong factor in the successful application of environmental inhibitors.

By far the most applicable and successful condition for prevention of red water and tuberculation is the natural occurrence or controlled production of a stable or a supersaturated water with respect to calcium carbonate. This is not always a cure-all. There are limitations. Some of the limiting factors have been mentioned, such as velocity of flow and minimum concentrations of calcium and alkalinity. Protection by a calcium carbonate film or coating must be complete, or tuberculation will occur. Partial protection can be worse than no protection, from the standpoint of carrying capacity, even though partial protection may reduce red water to a considerable extent.

The fact that this or any control must be *supplementary* to other measures is emphasized by the sheer quantity of calcium carbonate required to form a film on bare metal. For a city of 25,000 population it has been estimated that the internal surface of the distribution system is about 17 acres or 740,000 sq ft. A deposit of 0.001 in. uniform thickness would require 62 cu ft or 5.3 tons of calcium carbonate. If a deposition of 3 ppm from 3 mgd of supersaturated water were obtained, a period of 5 months would be required for a 0.001-in. thickness. If 99.9 per cent of the surface were protected by coating, however, so that inhibitor protection from the above water (at adequate velocity) were necessary only at the unavoidable flaws, a few hours of exposure should be sufficient for initial protection of the pipe.

Using the same calculation, 1 mi of 12-in. main extension, 99.9 per cent coated, should require less than 10 min of flow at 4 fps for deposition of 0.001 in. $CaCO_3$ on the equivalent of 17 sq ft of exposure. Many who have tried to apply this control measure will recognize that the foregoing is an academic statement of the problem, involving an oversimplification of the facts. Deeper investigation is required to explain the extremes of success and failure that have attended calcium carbonate treatment.

Pretreatment

It should be quite evident that the corrosion process is dynamic and involved in the extreme. There is no single solution for every problem. Furthermore, in view of the limitations imposed upon the control measures mentioned above, the more physical protection afforded by coatings, the less chemical control is needed. In addition, unavoidably exposed areas can be protected by initial exposure to a water that is heavily laden with calcium and alkalinity. Pretreatment is not an unusual practice in the art of corrosion control. Special pretreatment is used frequently for new or cleaned boilers and for cooling water systems.

In-place Coating

The McCauley method for in-place coating over a short period of time has considerable merit for pretreatment, in that the preparation has a very high ratio of calcium and alkalinity to dissolved oxygen.[3] This smothers the corrosive action of oxygen before it can take effect. Appropriate chemical treatment is then practiced to prevent the solution of such coatings. This has much more promise of success than chemical control by the usual additives.

When corroded and incrusted water mains are cleaned it should be obvious that much of whatever coating was present is scraped off, thus exposing more bare metal surface to the water. For the majority of surface waters and softened well waters the capacity to protect is too low to prevent corrosion from taking place again, even though such waters may have adequate capacity to *maintain* a protected exposure. Relining is essential if the carrying capacity is to be maintained. Here again, the McCauley method may have some merit as an alternative to relining, but at this time it does not appear to have been perfected and simplified to a standard procedure. Much experimental work needs to be done in the field before the McCauley method can be an accepted practice. More recently Radziul has demonstrated success with similar applications of cement.

Minor Water Quality Implications

For lime-softened waters of low alkalinity and calcium concentrations approaching 50 ppm, the saturation index may have to be as great as 1.0 to 1.3 to maintain protection. This is largely due to the formation of soluble complexes of calcium and magnesium with bicarbonate and carbonate ions at pH levels above about 8.2. This decreases the effective alkalinity for precipitation of calcium and requires an increase of pH for saturation.

Open-air reservoirs tend to add CO_2 to water at high pH levels (increasingly at pH levels above 8) and to reduce the saturation index. Heavy chlorination with liquid chlorine for algae control at these reservoirs also tends to reduce the pH and the saturation index. Deadend difficulties may be overcome by application of caustic soda or soda ash to the discharge from these reservoirs.

Other Influences

In regard to other water quality factors that may influence chemical control, there have been several reports from the British Non-Ferrous Metals Institute suggesting that natural color or organics in water have an effect on corrosion rates. In one set of experiments with galvanized steel, a balanced synthetic water failed to protect the metal, but protection was achieved when organics extracted from a natural water of the same mineral composition were added to the synthetic water.

In the laboratories of the Illinois State Water Survey, a series of similar tests was made on clean cast-iron specimens. A 40 per cent reduction in corrosion rate was achieved by the addition of organic materials extracted from the Illinois River at a concentration of 2 ppm or equivalent to 2 color units. This synthetic water was similar to Lake Michigan water in mineral content, and the pH was maintained at a level of 0.2 units below the saturation pH of calcium carbonate. In another test, a 10-ppm level of silica was maintained in water of the same quality, and the corrosion rate was reduced by 75 per cent. It is important that these waters were near-protective. In previous tests, waters offering little or no protection did not respond to such treatments, even with higher concentrations of the inhibitors.

Color and silica are two natural ingredients in water that may serve as supplements to chemical control and assist in providing a more uniform and complete deposit of calcium carbonate. Often, this deposit need be no more than an invisible transparent film. Color and silicate can be removed or lost, at least in part, during the coagulation step in treatment, and this may help to explain why treated surface waters sometimes resist efforts to control corrosion by mere pH adjustment.

Residual aluminum in the treated water could also be a factor in the effectiveness of control by calcium carbonate stability. If the aluminum concentration is at the saturation solubility level for the pH of the plant effluent, any decrease in pH will reduce the solubility and may cause precipitation of aluminum hydroxide. Because of its hydrated porous nature, the development of a dense $CaCO_3$ may be prevented. With improved methods of analysis for aluminum, further investigation on this possibility is warranted. Postchlorination with liquid chlorine may also cause this precipitate to be a major deposit on distribution systems.

Another ingredient that may have an important influence on calcium carbonate control is magnesium. Calcium carbonate in colloidal or microscopic form normally has a slight negative charge. Black[2] has shown that this charge is reversed by magnesium ions. It may be asked whether this causes the particles to approach and adhere more strongly to the negative cathode metal surface—or whether this reversal of charge is more difficult to achieve in the presence of high sodium concentrations.

SUMMARY

Chemical control of corrosion must be considered as an alternative to a variety of consequences. It is most effective as a supplement to other protective measures. Because of the variety of water qualities and of environments it is subject to many interesting complications.

The application of chemical control may be limited by cost; its effectiveness may be limited by the nature of the distribution system. In the public water utilities, the range of measures for chemical control is limited by the undesirable effects that certain inhibitors have on quality.

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Chemistry of the Lime-Soda Process

By JOHN F. DYE (Deceased) and J. L. TUEPKER

The hardness of almost all water supplies is caused by the presence, in solution, of calcium and magnesium compounds. Other bivalent ions such as strontium, ferrous iron, and manganese may contribute to the hardness to a lesser degree. The anions with which these bivalent ions are associated are principally the bicarbonate and sulfate ions, although chlorides and nitrates of calcium and magnesium do occur in some natural waters. The softening process consists of removing a part of these salts from the water to reduce the hardness to a predetermined value consistent with the reduction of detergent consumption, the control of scale formation, the prevention of corrosion, and other factors which make for a high-quality water. Calcium and magnesium bicarbonates are designated as "carbonate hardness," and calcium and magnesium sulfates (or chlorides and nitrates) are called "noncarbonate hardness."

The alkalinity determination on raw water ordinarily measures the carbonate hardness, but in some raw and softened waters the alkalinity may also include some sodium alkalinity if the total alkalinity exceeds the total hardness. Sodium alkalinity is often termed "negative noncarbonate hardness," since on reacting with lime, sodium carbonate is formed which is used for removing noncarbonate hardness. The noncarbonate hardness is measured by the difference between the total hardness and the carbonate hardness and requires soda ash for its reduction or removal. The sum of the alkalinity plus the noncarbonate hardness equals total hardness if the water contains no sodium alkalinity.

The chemistry of water softening is probably best explained or illustrated by showing the chemical reactions that take place when lime and soda ash are added to water containing calcium and magnesium salts. The reactions in the lime-soda process, then, are:

$$CO_2 + Ca(OH)_2 = CaCO_3\downarrow + H_2O \qquad (1)$$

$$Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3\downarrow + 2H_2O \qquad (2)$$

$$Mg(HCO_3)_2 + Ca(OH)_2 = CaCO_3\downarrow + MgCO_3 + 2H_2O \qquad (3)$$

$$MgCO_3 + Ca(OH)_2 = CaCO_3\downarrow + Mg(OH)_2\downarrow \qquad (4)$$

$$2NaHCO_3 + Ca(OH)_2 = CaCO_3\downarrow + Na_2CO_3 + 2H_2O \qquad (5)$$

$$MgSO_4 + Ca(OH)_2 = Mg(OH)_2\downarrow + CaSO_4 \qquad (6)$$

$$CaSO_4 + Na_2CO_3 = CaCO_3\downarrow + Na_2SO_4 \qquad (7)$$

These equations show all of the reactions taking place in softening a water containing both carbonate and noncarbonate hardness by the lime-soda process. It should be noted that, in Eq. (1), the carbon dioxide is not hardness as such, but in proportion to its content in the water will consume lime and must therefore be considered in calculating the amount of lime required. Similarly, in Eq. (5), the sodium bicarbonate or sodium alkalinity, if present, is not part of the hardness but, since it is included in the total alkalinity, it will consume lime. Eqs. (2) to (4) show the removal of carbonate hardness by lime. Whereas only one molecule of lime is required for one molecule of calcium bicarbonate, Eq. (2), two molecules of lime are required for the removal of one molecule of magnesium bicarbonate, Eqs. (3) and (4). Equation (6) shows the removal of magnesium noncarbonate hardness, usually magnesium sulfate, by lime. No softening is effected by this reaction because, for each molecule of magnesium noncarbonate hardness removed, an equivalent amount of calcium noncarbonate hardness is formed. Equation (7) shows the removal of calcium noncarbonate hardness, usually calcium sulfate, either originally in the water or formed as shown in Eq. (6).

From these reactions it is apparent that the amounts of lime and soda ash required to soften a water may be calculated from the concentrations of free carbon dioxide, bicarbonate (usually the total alkalinity), magnesium hardness, and noncarbonate hardness. Various equations have been proposed for calculating dosages of lime and soda ash. However, since free carbon dioxide is usually determined as mg/l of CO_2, and the alkalinity and various kinds of hardnesses are determined as mg/l of equivalent calcium carbonate, it is simpler to leave these terms in these forms.

To remove carbonate hardness and magnesium:

$$\text{lb } 100\% \text{ CaO per million gal} = 10.6 \times \text{mg/l } CO_2 + 4.7x \text{ mg/l alkalinity} + 4.7x \text{ mg/l magnesium hardness} + x \quad (8)$$

where x is the desired excess hydroxide alkalinity.

To remove noncarbonate hardness:

$$\text{lb } 100\% \text{ } Na_2CO_3 \text{ per million gal} = 8.8 \text{ mg/l noncarbonate hardness} - x \quad (9)$$

where x is the noncarbonate hardness to be left in the water.

These formulas are based on pure chemical compounds. The better commercial grades of high-calcium quicklime contain about 88 to 95 per cent available CaO; high-calcium hydrated lime contains approximately 68 to 70 per cent CaO. Commercial soda ash contains 99 to 100 per cent Na_2CO_3. The results from Eq. (8) should be divided by the per cent CaO in the lime used and multiplied by 100. If the exact analysis of the quicklime is not known, the results may be divided by 0.90, and for hydrated lime by 0.68.

Temperature, reaction-zone efficiencies, time, and catalytic effect of retained slurries will influence the completeness of reactions, and the stoichiometric calculations shown above will have to be adjusted to meet plant conditions.

An alternative method in the lime-soda process that should be mentioned here is the use of caustic soda instead of soda ash. The reactions of caustic soda with the carbonate and noncarbonate hardness are:

$$CO_2 + 2NaOH = Na_2CO_3 + H_2O \quad (10)$$

$$Ca(HCO_3)_2 + 2NaOH = CaCO_3\downarrow + Na_2CO_3 + 2H_2O \quad (11)$$

$$Mg(HCO_3)_2 + 4NaOH = Mg(OH)_2\downarrow + 2Na_2CO_3 + 2H_2O \quad (12)$$

$$MgSO_4 + 2NaOH = Mg(OH)_2\downarrow + Na_2SO_4 \quad (13)$$

Equations (10), (11), and (12) show that caustic soda removes free CO_2 and carbonate hardness and in so doing forms an equivalent amount of sodium carbonate, which reacts with the noncarbonate hardness according to Eq. (7).

Liquid caustic soda (50% NaOH) is usually used. The advantages are: ease of handling and feeding, lack of deterioration in storage, and the fact that less calcium carbonate sludge is formed.

The advisability of using caustic soda instead of soda ash in the lime-soda process depends on comparative delivered costs of the three chemicals and the analysis of the raw water. As can be seen from the above equations, caustic soda performs a double duty in precipitating both carbonate and noncarbonate hardness and, therefore, it may be used not only in the place of soda ash but as a substitute for part or all of the lime requirement.

VARIATIONS IN THE LIME-SODA PROCESS

Before the chemistry of the lime-soda process was completely understood, the hardness reduction obtained by its use was often unsatisfactory, and even where the hardness reduction was satisfactory, deposits in mains and pipes through which the soft water passed resulted in many complaints as to its quality. This led to the development and adoption of methods designed to prevent scale formation by improving the stability of the softening plant effluent. These methods include: carbonation after conventional lime-soda treatment; excess-lime treatment, either followed by recarbonation or with split treatment; the use of coagulants containing aluminum; the use of activated silica; the use of coagulant aids; sludge recirculation; suspended-solids contact softeners; the use of polyphosphates to inhibit calcium carbonate scale formation; and the substitution of cation exchangers for soda ash to remove noncarbonate hardness. Since hard waters may vary widely in composition, any one or several of these modifications may be used to produce a non-scale-forming, noncorrosive soft water.

The effect of adding lime to raw waters of various compositions is shown in Fig. 1. The changes in alkalinity and in calcium, magnesium, and noncarbonate hardnesses when increasing amounts of lime are added to waters with different ratios of alkalinity to hardness are demonstrated graphically by these curves. A study of the curves reveals the economy in lime consumption for the reduction of calcium hardness to the desired level as compared to the lime required to reduce the magnesium hardness to its optimum level. In general, these curves point out the reasons for the variations in lime treatment described below.

Conventional Lime–Soda Ash Softening Followed by Recarbonation

When it is not necessary to remove practically all the magnesium hardness or when the raw water is low in magnesium hardness so that special methods are not needed for its reduction, treatment with just enough lime to precipitate the carbonate hardness may be used. This is often called "selective calcium carbonate removal." If it is desired to reduce the carbonate to the minimum, enough lime should be added to obtain the pH of maximum carbonate ion concentration. This pH value varies with temperature and total alkalinity as shown in Fig. 2, and at this point twice the phenolphthalein alkalinity equals the total alkalinity, or $2P = T$. Soda

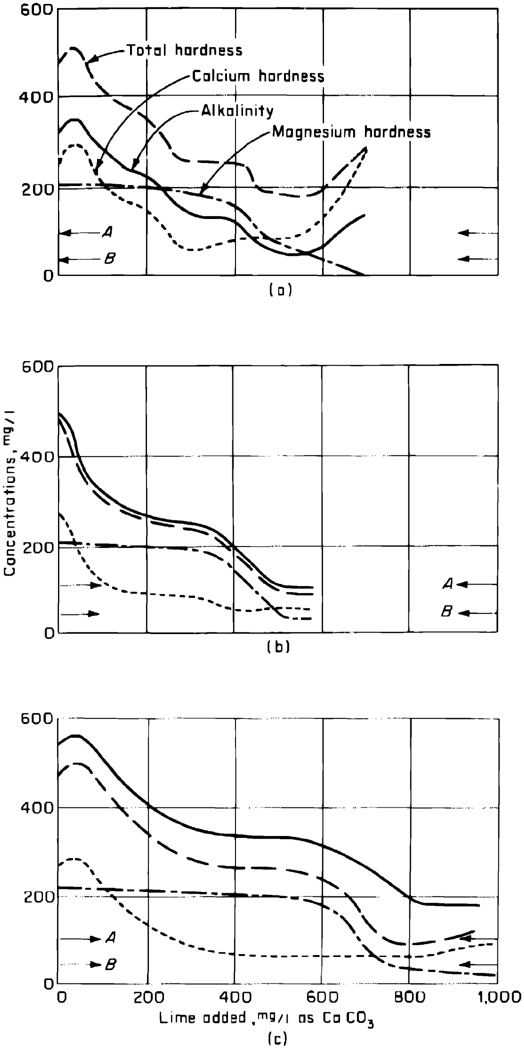

Fig. 1 Effect of addition of lime in reducing the alkalinity and the magnesium, calcium, and total hardnesses under various conditions of alkalinity and hardness. Solid, dashed, dashed and dotted, and dotted curves represent alkalinity, total hardness, magnesium hardness, and calcium hardness, respectively. Parts *a*, *b*, and *c* represent the following conditions: Part *a*—total hardness exceeds alkalinity; part *b*—total hardness and alkalinity are equal; part *c*—alkalinity exceeds total hardness. Levels *A* and *B* represent desired total hardness and magnesium hardness, respectively. All concentrations are expressed as $CaCO_3$. (*After Larson, Lane, and Neff.*[1])

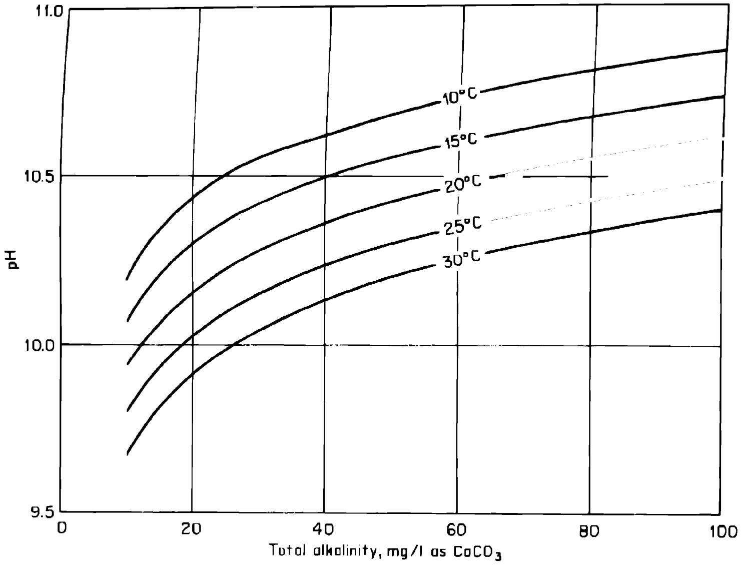

Fig. 2 Variation of pH of maximum carbonate ion concentration with total alkalinity at several temperatures.

ash may or may not be required, depending on the amount of noncarbonate hardness present in the raw water. Sludge recirculation may be used to aid in calcium carbonate precipitation, and recarbonation is usually practiced to produce a stable effluent. Often sodium polyphosphates are also used to inhibit incrustation of the filter sand and scale formation in the distribution system. Although extremely low hardnesses are not usually required or desirable for municipal use, by this method the calcium carbonate hardness may be reduced to 15 to 20 mg/l.

Excess-lime Treatment

With waters containing more than about 40 mg/l magnesium hardness (as $CaCO_3$) it is usually necessary to resort to excess-lime treatment to obtain the desired magnesium reduction. Since it is not good practice to pump highly caustic water to consumers, some means must be used to neutralize the excess lime remaining in solution after settling out the precipitated magnesium hydroxide and calcium carbonate in the primary basin. The easiest method is to convert it to calcium carbonate by recarbonation or by the use of bypassed raw water ("split treatment").

Figure 3 illustrates the magnesium reduction obtained in the primary basin in one plant with various hydroxide alkalinities. Note that these hydroxide alkalinities are total—not excess. Thus, while a reduction to

40 mg/l is obtained by a total hydroxide alkalinity of 54 mg/l, the excess hydroxide alkalinity required is 54 minus 40, or only 14 mg/l. Also it should be noted that a curve based on the solubility product K_{sp} for magnesium hydroxide would be appreciably lower, and other plants may obtain a closer approach to the theoretical solubility than the plant results illustrated in Fig. 3.

Excess Lime Followed by Recarbonation

It has been found that when a water softened by the lime–soda ash method contains magnesium hardness of 40 mg/l or less (as $CaCO_3$), there will be no trouble with magnesium hydroxide scale in ordinary domestic hot-water heaters operated at 140 to 150°F. Therefore, if the hard water contains magnesium hardness in excess of this amount, an effort should be made to reduce it to 40 mg/l or less. To do this, treatment with an excess amount of lime is usually necessary. After the precipitated magnesium hydroxide and calcium carbonate have settled, but before filtration, the water is recarbonated to convert the excess calcium hydroxide to calcium carbonate and again flocculated and settled. The procedure is as follows:

1. Add 10 to 45 mg/l of lime in excess of the quantity theoretically required to combine with the free carbon dioxide, bicarbonate alkalinity, and magnesium. Twice the phenolphthalein alkalinity minus the total alkalinity may be 40 to 70 mg/l, depending on the composition of the raw water, temperature, and plant design. Usually, a hydroxide alkalinity of 50 to 60 mg/l is sufficient. The use of alum or sodium aluminate as a coagulant often makes it possible to obtain sufficient reduction of magnesium with hydroxide alkalinities of only 30 to 40 mg/l.

2. Settle out the precipitated calcium carbonate and magnesium hydroxide.

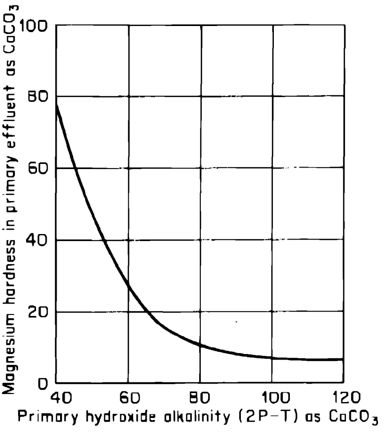

Fig. 3 Effect of hydroxide alkalinity (2*P*-*T*) on amount of residual magnesium hardness in primary basin in one lime–soda ash softening plant.

3. Recarbonate with carbon dioxide gas to the point where the total alkalinity equals twice the phenolphthalein alkalinity. The pH value at this point is approximately 10.4, although this pH of maximum carbonate-ion concentration varies with total alkalinity and temperature, as shown in Fig. 2.

4. Add any soda ash required for the removal of noncarbonate hardness; mix; flocculate, using recirculated calcium carbonate sludge, if necessary, to aid precipitation; and settle.

5. A water softened in this manner will have a pH of about 10.9 and will have scale-forming tendencies. It may be stabilized by recarbonating to a pH of 9.7 to 10.0 and by the addition of about 0.25 to 0.5 mg/l of a sodium polyphosphate.

6. Filter through sand. The application of 0.25 to 0.50 mg/l of sodium polyphosphate to the applied water will prevent incrustation of the filter sand.

In this procedure, the process of recarbonation requires close supervision to obtain the desired results. In some instances, recarbonation to the point of maximum carbonate-ion concentration results in total alkalinities that are too low, in which case a slight overcarbonation is desirable. A final total alkalinity of 35 to 50 mg/l containing 15 to 25 mg/l of bicarbonate alkalinity is preferable for corrosion prevention to one of 20 to 25 mg/l that is all carbonate.

In the above procedure, it is recommended that any soda ash required be added after recarbonation for the reason that the magnesium hydroxide precipitated in the primary treatment often adsorbs an appreciable amount of negative ions, thus reducing the noncarbonate hardness. To obtain the full effect of this adsorption, it is best to add the soda ash after the magnesium hydroxide has settled. Since the noncarbonate hardness is often reduced by as much as 10 per cent in this way, it often obviates the use of small dosages of soda ash.

Split Treatment

Split treatment consists of treating a large portion of the hard water with all the required lime and then, after settling the precipitated magnesium hydroxide and calcium carbonate, of adding the balance of the hard water and again mixing and settling. Adding all the lime requirement to only a portion of the water results in excess lime treatment for this fraction, with the result that practically all of its magnesium content is removed. This excess lime is then neutralized by the free carbon dioxide and bicarbonate alkalinity in the bypassed water, thus removing calcium hardness from it.

The magnesium hardness in the larger portion of the raw water may be reduced to less than 10 mg/l in the primary treatment. The addition of the bypassed hard water reintroduces some magnesium, but if a careful selection is made of the ratio of the amount of water to be treated with excess lime to the amount of water to be bypassed to the secondary treatment, magnesium hardnesses of less than 40 mg/l can usually be obtained.

The proper proportions of raw water to be treated with lime and to be bypassed can be ascertained by analysis of the raw water and, if possible, by preliminary experiments in softening the water with lime. Since plant operation will not duplicate perfectly the results obtained in small-scale experiments, some experimentation is necessary when a split-treatment plant is first placed in operation.

In order to calculate the optimum percentage of raw water to bypass, the following information is required, all in terms of mg/l equivalent calcium carbonate:

1. Raw-water alkalinity
2. Raw-water free CO_2 (mg/l free $CO_2 \times 2.27$)
3. Raw-water magnesium hardness
4. Bicarbonate alkalinity desired in plant effluent
5. Hydroxide alkalinities in primary basin effluent
6. Magnesium hardnesses obtained with these hydroxide alkalinities in the primary treatment

Make a plot using hydroxide alkalinities as abscissas and primary residual magnesium hardnesses as ordinates to obtain a softening curve (Fig. 3). Using values from this curve, calculate the optimum percentage of raw water to bypass for the desired magnesium hardness and bicarbonate alkalinity in the plant effluent by the following equations:

Per cent raw water to bypass =

$$\frac{100(\text{primary OH alkalinity} + \text{desired bicarbonate alkalinity})}{\text{Primary OH alkalinity} + \text{raw total alkalinity} + \text{raw free } CO_2} \qquad (14)$$

The magnesium hardness in the plant effluent is the weighted average of the magnesium hardnesses in the primary effluent and the raw water, or

Effluent magnesium hardness =

$$\frac{(\%\text{ Bypass} \times \text{raw Mg hardness}) + (100 - \%\text{ bypass}) \times \text{primary Mg hardness}}{100} \qquad (15)$$

As an example, at the plant at which the data for Fig. 3 were obtained, the raw water magnesium hardness is 133, total alkalinity 313, and free carbon dioxide 68, all as mg/l equivalent $CaCO_3$. Using these values and the data from Fig. 3, and assuming that it is desirable for the plant effluent to contain 15 mg/l of bicarbonate alkalinity and substituting these values in Eqs. (14) and (15), the curves shown in Fig. 4 were developed. Curve *A* shows the plant effluent magnesium hardness that would be obtained when neutralizing the primary hydroxide alkalinities with the per cent bypassed

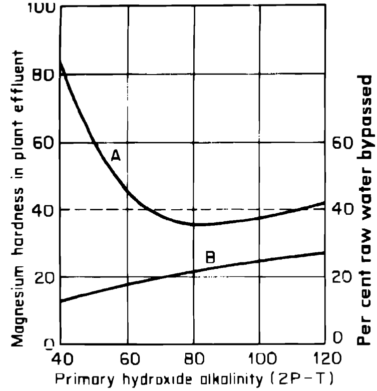

Fig. 4 Calculated per cent of raw water to bypass and the resulting magnesium hardness in the plant effluent for various hydroxide alkalinities in the primary basin effluent for split treatment of a water with the following characteristics: alkalinity, 313 mg/l; free CO_2, 68 mg/l; magnesium hardness, 133 mg/l; all as $CaCO_3$. Bicarbonate alkalinity desired in plant effluent, 15 mg/l. Data for residual magnesium hardnesses at various hydroxide alkalinities obtained from Fig. 3. Equations (14) and (15) used for calculations. Curve *A*: per cent raw water to bypass. Curve *B*: magnesium hardness in plant effluent.

raw water shown in curve *B*. Magnesium hardness in the plant effluent would, theoretically, be reduced to 40 mg/l when about 82 per cent of the raw water is treated with enough lime to yield a primary hydroxide alkalinity of 66 mg/l (or an excess hydroxide alkalinity of 26 mg/l). In actual practice at this plant, when bypassing 22 per cent of the raw water to neutralize a primary hydroxide alkalinity of 80 mg/l, the magnesium hardness in the secondary is 38 mg/l.

The curve shown in Fig. 3 is an example of a softening curve for magnesium obtained at one plant and should not be used as a reference for magnesium reduction at all plants. The values will vary from plant to plant depending on reaction and settling time, coagulants or coagulant aids used, if any, and temperature. Several curves should be prepared for the different conditions which might be encountered.

These calculations make it possible to decide upon the advisability of using split treatment with a given water, since the magnesium hardness obtainable by this method can be determined. Split treatment is not necessarily the best and most economical treatment for all high-magnesium raw waters. Its suitability for such waters depends on the amount of raw-water alkalinity and free carbon dioxide available for neutralization of the hydroxide alkalinity in the primary effluent and the magnesium concentration in the raw water which governs the amount of magnesium hardness reintroduced when the primary effluent and bypassed raw water are blended.

A variation of the split treatment can be used if there is a slight deficiency of bicarbonate alkalinity and free carbon dioxide in the raw water. Some carbonation of the primary effluent or the blended water can be used as a supplement. This is in effect the same as increasing the free carbon dioxide content of the raw water.

By the use of split treatment, the maximum efficiency in the use of lime is obtained, since no excess over the theoretical lime requirement is necessary, and in Eq. (8), x becomes 0. Soda ash, if required, should be applied to the secondary basin, and the use of sludge recirculation and the addition of the polyphosphate after the secondary settling or final recarbonation after filtration may be advisable just as in the method using excess lime followed by recarbonation.

Three-stage Treatment

A growing number of lime–soda ash softening plants are reburning the sludge produced as a method of solving, at least partially, the problem of sludge disposal. Where conventional softening is used and the sludge consists principally of calcium carbonate, a high quality of lime is obtained, which is again used for softening. However, where either of the excess-lime treatments is used, the magnesium content of the sludge increases, and the quality of the lime made from it deteriorates. One method that is being used to eliminate the magnesium is the process suggested by the late Charles P. Hoover.[21] With this process, the primary treatment is subdivided and, in the first stage, adds only that lime required by the free CO_2 and bicarbonate alkalinity of the water, with perhaps a very slight excess to precipitate a small amount of magnesium hydroxide to act as a coagulant. After settling, this practically pure calcium carbonate sludge is pumped to the lime reburning plant. The effluent from the first stage passes to the second stage where more lime is added to provide the hydroxide alkalinity required for the desired reduction in magnesium hardness. The sludge from the second stage contains not only magnesium hydroxide, but also some calcium carbonate, which precipitates when the calcium ion concentration is increased upon the addition of more lime. However, because of the preponderance of magnesium hydroxide, the sludge particles are quite light, and to prevent carryover of magnesium hydroxide to the last stage the per cent solids in the second stage sludge must be controlled to meet hydraulic conditions within the treatment unit. Also, it has been found that this light magnesium floc may be weighted by recirculating a small amount of calcium carbonate sludge from the third stage back to the second-stage quick-mix basin. This is a very economical coagulant aid. This second-stage sludge may be pumped to a pond, or it may be recarbonated to redissolve most of the suspended solids, using waste gases from the lime-reburning plant for this purpose. The effluent from the second stage goes to the third or final stage where it is recarbonated or mixed with bypassed raw water, depending on which method of softening is being used.

In at least one plant which has excess-treating capacity for high summer rates, the installation of the necessary sluice gates provided the needed flexibility so that three-stage split treatment could be used for 8 or 9 months of the year and two-stage split treatment for the other 3 or 4 months of the year. The reburned lime produced while three-stage treatment is used has an available calcium oxide content of 93 to 95 per cent, whereas, while two-stage treatment is being used, the per cent available calcium oxide varies from 83 to 85 per cent. Although some calcium carbonate is wasted in the second stage, with three-stage treatment, this is more than compensated for by the almost 100 per cent recovery of solids from the sludge in the lime-reburning plant. When high-magnesium sludge is centrifuged before reburning, the centrifuge is adjusted to eliminate a large portion of the magnesium hydroxide, and this carries with it considerable calcium carbonate. A high–calcium carbonate sludge, however, only needs to be dewatered, and practically all of the calcium carbonate is recovered.

Cation Exchangers for Removal of Noncarbonate Hardness

Where salt may be obtained at a low cost, it is sometimes more economical to remove noncarbonate hardness by means of cation exchangers than by soda ash. However, the analysis of the water to be softened, as well as the cost of salt and of the additional equipment required, must be taken into consideration.

With this method, the water is first treated with lime to convert all free carbon dioxide and bicarbonate alkalinity to normal carbonates. After mixing and flocculating, the precipitated calcium carbonate is settled out. A very small amount of magnesium hydroxide is also removed in this step, but the greater part of any magnesium present remains in solution. After settling, the lime-softened water is carbonated with carbon dioxide gas to convert most of the normal carbonates to bicarbonates. The pH should be reduced at least to the pH of the water after lime softening to prevent deposition of calcium carbonate on the cation-exchange material. From the carbonation basins the water flows to sand filters, and then, depending on the final hardness desired, all or part of the water is passed through cation-exchange softeners. For some industrial uses, especially steam generation, a low alkalinity in the finished water is desirable, and for this purpose neutralization of very nearly half of the carbonate alkalinity with sulfuric acid is preferable to carbonation with carbon dioxide gas.

Details of the cation-exchange process of water softening are given later in this chapter.

INCIDENTAL BENEFITS OF LIME SOFTENING

The fact that lime softening has a marked bactericidal effect was first noted by Houston in England in 1912.[5] This was confirmed by Hoover at Columbus, Ohio, the next year[6,7] and has been studied in detail by other investigators since then.[8-12] In general, the higher the pH value obtained in the treatment, the greater the per cent kill of organisms. There is a marked difference in the per cent kill as the pH is increased from 9.5 to 10.5 and above. The pH values obtained in excess-lime treatment are usually above 11.0, and in this pH range the kill is practically 100 per cent in less than 2 hr, even at low temperatures. However, regardless of the effectiveness of lime as a bactericidal agent, it should not be used as a substitute for chlorination of contaminated waters.

In the softening of uncontaminated well waters, where excess-lime treatment is used, an appreciable reduction in chlorine dosage is effected if the chlorine is applied to the secondary basin influent to take advantage of the reduction in chlorine demand by the high lime dosage. This is particularly true if the well water has a high ferrous iron content, since this often accounts for most of the chlorine demand in a well water.

An incidental benefit of lime softening is the complete removal of iron. This is seldom the reason for the installation of a lime softening plant, but the objection to the high iron content of many well waters is almost as great as the objection to the high hardness.

Disposal of Lime-softening Sludge

Disposal of the large quantities of sludge formed in lime–soda ash softening plants is a serious problem and must be planned in advance. The principal methods used are: (1) discharge into water courses, (2) discharge into sewers, (3) ponding or lagooning, (4) filtering in a vacuum filter and using the resultant cake for land fill or as agricultural lime, and (5) recalcination of the dewatered, dried sludge.

The discharge of water-softening sludge into streams is still practiced by about 50 per cent of the softening plants, but many states are discouraging this method of sludge disposal not only because of the unsightly condition created but also because it is detrimental to aquatic life.

Many plants discharge the sludge into sewers. In the 1949 AWWA committee report[2] it appears that in some cities this is not permitted since it has been found to stop digestion of the sewage, while in others it has been found to be beneficial. In one city there is an ordinance which forbids discharging to the sewers any wastes with a pH value of more than 10.0 or with a total solids content of more than 1,000 ppm. Local authorities should be consulted if such a means of sludge disposal is contemplated.

The use of sludge beds or lagoons is also quite common, and where land is available for such a purpose, this is an economical method of disposal. At least three lagoons should be used so arranged that they can be used alternately and so designed that the supernatant can be drained. Each lagoon should be large enough to hold a year's production of sludge. When operated on a "fill and let dry" basis, the sludge will concentrate to about 50 per cent moisture, and an applied sludge with 90 per cent moisture will concentrate to about 16 per cent of its original volume.[3] When properly constructed and managed, lagooning of water-softener sludge is a practical method of disposal.

In at least two plants vacuum filters have been used successfully to concentrate softening plant sludge.[2,4] Although the moisture content of the filter cake is at least as high as, if not higher than, the dried sludge in lagoons, it appears that no great difficulty is encountered in the handling of the cake, and in one case, farmers are making use of it for agricultural lime.

The latest and perhaps the most interesting method of lime-sludge disposal is reburning the sludge to make quicklime for reuse in the softening process. The methods that have been used are: (1) multiple-hearth kilns, (2) flash calcining of the dried and powdered sludge, (3) rotary kilns and (4) fluo-solids reactors. Of these methods, the last two are the most successful.

Rotary kilns are now in continuous operation for calcining water-softener sludge at Miami, Florida; Dayton, Ohio; and at San Diego, California. A fluo-solids reactor has been operated successfully at Lansing, Michigan, since 1955. The fluo-solids reactor has a slight advantage in space, labor requirements, and fuel consumption, but the cost of lime produced in either the rotary kiln or fluo-solids reactor compares favorably with the cost of purchased lime and, in addition, the problem of sludge disposal is eliminated or very greatly reduced.

EQUIPMENT REQUIRED FOR LIME–SODA ASH SOFTENING

The equipment required for lime–soda ash softening is similar to that used in water-filtration plants and includes: rapid mixing, flocculating, and sedimentation basins; chemical handling and feeding equipment; conventional rapid-sand filters; and, if needed, some form of carbon dioxide–generating equipment. The laboratory facilities provided should be as extensive as possible in order to allow complete control tests to be made at each step in the softening process.

Rapid-mix, Flocculation, and Sedimentation Basins

The softening process may be carried out in conventional rapid-mix, flocculation, and sedimentation basins or in solids-contact softeners which embody in a single unit the necessary mixing, flocculating, and settling. In conventional lime–soda ash softening plants, mechanical mixers are preferred for rapid mixing and flocculating, since it is desirable to have the degree of agitation independent of the rate of flow through the basins. The rapid-mix basin has two purposes: (1) to dissolve the rather insoluble slaked lime, and (2) to thoroughly mix the lime with the water and start the chemical reactions. A 5- to 10-min period is sufficient for this purpose. In the flocculation basin, on the other hand, chemical reactions are being completed, and precipitation and floc growth are promoted. These processes are relatively slow, and it has been found that some 40 to 60 min are generally required for this purpose. Since precipitation of calcium carbonate and magnesium hydroxide takes place more readily on the surface of previously formed particles, the recirculation of sludge to the rapid-mix basin is usually a distinct aid. In addition, it has been found that if there are enough centers of crystallization in the water, there is less precipitation on the walls and agitator paddles, and the amount of basin cleaning required is lessened appreciably.

The retention time in the sedimentation basins should be 2 to 4 hr, depending on the character of the flocs or suspended matter and the kind of coagulant or coagulant aid used. To avoid eddy currents and short circuiting, horizontal velocities of not over 0.5 to 1.0 ft per minute are used. Straightening baffles are sometimes desirable at the inlet to distribute the flow evenly over the cross section of the basin. Because of the large volume of sludge produced in lime–soda ash plants, mechanical sludge collectors are commonly used. However, even with their use, the volume of the settled sludge should be considered in calculating the required basin volume.

The large amounts of chemicals used in lime–soda ash softening plants necessitate storage bins large enough for at least one month's supply of each chemical. This often makes it possible to purchase the chemicals in bulk carload lots. Mechanical or pneumatic unloading and conveying equipment permits economical handling of the chemicals. Elevated storage bins provide gravity flow to the chemical feeders.

Chemical Feeders

The most important items of chemical feeding equipment are the lime feeder and the slaker. Gravimetric feeders weigh the lime as it is fed into the slakers and are usually equipped with temperature regulators and alarms which protect against excessive slaker temperatures and appreciable underfeeding and overfeeding. Now available are feeders which proportion the lime feed to the water to maintain the correct dosage regardless of raw-water influent rates. Also available are overriding pH controls which will make small changes in the dosage to compensate for variations in the composition of the raw water and purity of the lime. Most modern slakers are supplied with grit removers for the removal of coarse, inert material from the slurry before it is fed to the quick-mix basin.

Two types of slakers are available: the retention type and the newer paste type. In the retention type, the ratio of water to lime is 4: or 5:1, 20 to 30 min being required to slake the lime. Built-in heat exchangers are often supplied for warming the incoming slaking water. Paste-type slakers use a lower ratio of water to lime, usually 2: or 2.5:1, and slake at near-boiling temperatures. The higher temperature accelerates the slaking process so that the slaking time is usually less than half of that required in a retention-type slaker. The paste of slaked lime is diluted and passed through a grit remover to remove objectionable insolubles before being fed into the water. A more complete discussion of lime slakers and their operation is given in Chapter 17.

Dry feeders for soda ash, alum, ferrous or ferric sulfate, or coagulant aids may be required. These feeders should be located directly below the storage bins. Liquid coagulants have become quite popular because of the ease of controlling the dosage by the use of metering pumps. Since these solutions are usually quite corrosive, the pumps, valves, and piping must be constructed of suitable corrosion-resistant materials.

Filters and Appurtenances

The filters and appurtenances used in lime-soda ash softening plants are identical with those used in conventional rapid-sand filter plants. There are, however, some special problems to consider and precautions to take. The turbidity of the applied water is usually considerably higher than in a conventional filter plant and often consists of fine calcium carbonate crystals rather than a floc turbidity. This fine calcium carbonate may penetrate the filter sand to a considerable depth, especially as the loss of head builds up near the end of the filter run. This necessitates very complete backwashing, since any fine calcium carbonate left in the sand bed may, in time, promote its cementation. The use of some type of surface-wash system is highly recommended for keeping the filter bed clean. It is good practice to produce a slightly scale-forming water, and incrustation and cementation of the filter sand by such a water can be prevented by the addition of a polyphosphate. This will also prevent unsightly deposits on the washwater troughs and filter walls. Because of the danger of clogging, porous underdrain systems are seldom used for lime-softened waters.

Washwater tanks or washwater pumps and piping should be sized to give a wash rate of 20 gpm/sq ft (approximately 36-in. rise rate per minute) for at least 10 min. This abnormally high rate can be beneficial when attempting to remove accumulated calcite crystals from the filter bed. It does not appear to be feasible to specify a sand expansion rate, because this can vary with the porosity and effective size of the filter media. The importance of backwashing should be based on effective removal of accumulated material in the sand regardless of sand size.

Since the water used for backwashing is treated and filtered water, it is uneconomical to waste it. A washwater cistern large enough to receive the water from at least one filter wash should be provided. Automatically controlled pumps should be furnished to return this washwater, together with any sludge it contains, to any flocculation basin. Since this cistern will require occasional cleaning, the bottom should slope to a sump, from which any accumulated sludge or sand can be removed.

Sludge-handling Pumps

Sludge-handling pumps must be provided for sludge recirculation, and for sludge disposal if gravity drains cannot be used. The capacity of the sludge-disposal pumps should be based on pumping a sludge that is as low as 5 per cent solids by weight. The actual amount to be pumped depends on the maximum influent rate expected and the analysis of the water to be treated. To avoid wastage of water, provision should be made for throttling the pumps at rates lower than the maximum and for pumping a heavier sludge if so desired. Centrifugal pumps, preferably the open impeller types, are commonly used. With this type of pump, no difficulty has been found in pumping sludges up to 15 per cent by weight over distances of 2 to 3 miles or more.

For sludge recirculation it is preferable to use a slow-speed centrifugal pump or a torque-type pump, so that the breakup of flocculated solids will be held at a minimum. Large diaphragm- or plunger-type pumps are also used for this purpose. Since the amount of sludge recirculated is usually important, provision must be made for throttling if centrifugal pumps are used or for changing the length of stroke or pump speed if positive-displacement pumps are employed.

RECARBONATION

Chemistry of Recarbonation

Recarbonation is used for two purposes in a lime-softening plant: (1) for pH adjustment, and (2) for the neutralization and precipitation of the calcium hydroxide in the primary basin effluent in cases where high-magnesium waters are softened by application of excess lime followed by recarbonation. When a low-magnesium hard water is treated with the amount of lime necessary to react with the free CO_2 and bicarbonates, as in the process of selective calcium carbonate removal, the water remains supersaturated with calcium carbonate and may have a pH as high as 10.4 or more. This water would be highly encrusting, and the pH should be adjusted downward before filtration. Carbon dioxide gas is bubbled through the water for this purpose. The carbon dioxide combines with all or a part of the unprecipitated calcium carbonate to form some soluble bicarbonate, the amount depending on the final pH desired. The reaction is:

$$CaCO_3 + CO_2 + H_2O = Ca(HCO_3)_2 \qquad (16)$$

If enough lime has been added to precipitate some magnesium hydroxide, the hydroxide alkalinity which remains must also be converted to bicarbonate according to the following reaction:

$$Ca(OH)_2 + 2CO_2 = Ca(HCO_3)_2 \qquad (17)$$

If, however, the method of excess lime followed by recarbonation is used, there is too much calcium hydroxide present after sedimentation, and converting it to the soluble bicarbonate would unduly increase the hardness. It is necessary to precipitate it as calcium carbonate according to the reaction

$$Ca(OH)_2 + CO_2 = CaCO_3\downarrow + H_2O \qquad (18)$$

Sometimes it is possible to add enough additional carbon dioxide to convert a portion of the carbonate to the bicarbonate in the recarbonation basin between the primary and secondary basins and thus lower the pH to the desired figure, but because of the danger of redissolving some of the precipitated calcium carbonate, it is better to make a final pH adjustment by a final recarbonation just after filtration.

Equipment for Recarbonation

Carbon dioxide gas for recarbonation may be obtained in several ways. In the older plants, the gas is generated by burning a fuel such as coke, oil, or gas or a combination of these with an excess of air, scrubbing the stack gases, and then conveying the gas by means of a blower or compressor to the point of application. If the fuels are burned in a boiler, the steam generated may be used to drive the blower or compressor or for space heating. The scrubbers, compressors or blowers, control valves, and piping require considerable maintenance because of the corrosiveness of the moist gas. The percentage of carbon dioxide in the gas made in this way may vary widely, making frequent adjustment of the control valve necessary. There is also a health hazard, since some carbon monoxide is usually present in the gas.

The newer underwater burners, by the use of which a mixture of a gas such as propane and air is burned underwater near the bottom of the carbonation basin, are free from most of these difficulties since the amount of gas to be burned can be easily regulated. Smaller plants or those requiring only a slight pH adjustment may resort to the use of dry ice or liquid CO_2 and thus eliminate the combustion equipment, scrubbers, and compressors, and also the danger from carbon monoxide gas.

An evaporator is used to change the solid or liquid carbon dioxide to a gas which then passes through a pressure-regulating valve to the diffusers in the carbonation basin. The amount of carbon dioxide used may be controlled very exactly by the use of a rotameter. Since the gas is pure carbon dioxide, much smaller piping and diffusing equipment is needed than is required for carbon dioxide generated from fuels.

The carbonation basin should provide 15 to 30 min retention time and should be 10 to 15 ft deep to allow for complete absorption of the carbon dioxide. Recarbonation should not be done at the end of a sedimentation basin since the eddy currents set up by the bubbles of gas rising through the water preclude good sedimentation. The basin must be well ventilated or, preferably, open to the outside atmosphere. Equipment for testing for oxygen deficiency and carbon monoxide should be at hand.

The point of application of the carbon dioxide depends upon the method of softening used. In conventional plants, where selective calcium carbonate removal is used where just enough lime is added to convert all of the bicarbonates to the normal carbonate with little or no magnesium precipitation, carbonation of the water to at least partially stabilize it before filtration is best. The presence of any free CO_2 which would corrode the underdrain system may be avoided by making certain that the Langelier index for the water is slightly on the plus side. Incrustation of the filter sand may be avoided by the use of about 0.5 mg/l of a polyphosphate. Where excess-lime treatment is used to reduce magnesium hardness, it is necessary to add just enough carbon dioxide to convert the calcium hydroxide to insoluble calcium carbonate and settle as described on page 338. After this secondary settling it may be desirable to recarbonate further, either just before or immediately following filtration.

Carbonation through the use of carbon dioxide may not be necessary in plants that require coagulation or sizable quantities of chlorine. The acidity of the chlorine or the coagulant may serve the purpose of recarbonation.

PRODUCTION OF STABLE LIME–SODA ASH–SOFTENED WATER

In the early days of lime–soda ash softening of municipal water supplies it was soon found that loss of carrying capacity of the mains, due to heavy deposits of scale, was a serious problem. A long sedimentation period to reduce the supersaturation of the water with calcium carbonate was first resorted to, but the expense of large storage basins proved prohibitive in cost. The result was that few new municipal softening plants were built for a considerable period. While recarbonation of lime–soda ash-softened water had been tried unsuccessfully in 1901 at Winnipeg, Canada, and was proposed by George Whipple in 1905 as a corrective measure, it was not until 1921 that recarbonation was carried out successfully at a new plant at Defiance, Ohio.

At first, prevention of scale formation or afterprecipitation in the mains was the sole objective of recarbonation. However, it could be seen that overrecarbonation made the water corrosive, so that red-water troubles increased. Even when recarbonation was carefully adjusted so that all the carbonate was converted to the bicarbonate but no free carbon dioxide was present at a pH of 8.35, the water was still corrosive. As knowledge of water chemistry in general and of carbonate equilibria in particular increased, the present dependence on the deposition of a hard protective scale of calcite as a preventive measure against corrosion increased.

The application of some of the principles of physical chemistry, especially the law of mass action, to the interpretation of water analysis and carbonate equilibria culminated in the development of the calcium carbonate saturation index by Langelier.[13] Other developments followed which corrected for the shortcomings of the Langelier index, especially in the higher pH ranges. Several procedures and indexes have been proposed, all of them purporting to predict and measure the tendency of a water to deposit or dissolve calcium carbonate and thus its ability to protect against corrosion. Two of these, the marble test and Enslow's stability indicator, are practical laboratory methods for determining whether or not a water is in chemical balance with solid calcium carbonate. The other indexes are related to and derived from the following three mass law equations and one stoichiometric equation for electrical neutrality in a water solution:

$$\mathrm{Ca}^{++} \times \mathrm{CO}_3^{--} = K_s' \tag{19}$$

$$\frac{\mathrm{H}^{+} \times \mathrm{CO}_3^{--}}{\mathrm{HCO}_3^{-}} = K_2' \tag{20}$$

$$\mathrm{H}^{+} \times \mathrm{OH}^{-} = K_w' \tag{21}$$

$$\mathrm{Alk.} + \mathrm{H}^{+} = 2(\mathrm{CO}_3^{--}) + \mathrm{HCO}_3^{-} + \mathrm{OH}^{-} \tag{22}$$

Langelier's Calcium Carbonate Saturation Index

From the above equations, Langelier derived a formula for computing the pH of saturation, pH_s, of a water, at which pH, with no change in alkalinity, calcium content, or dissolved solids, the water would neither deposit nor dissolve calcium carbonate.[13] Since the pH_s of most lime-treated waters is below 9.0, the simplified form of Langelier's equation, applicable when the pH_s falls between approximately 6.5 and 9.5, can be used for lime-softening plant effluents. Expressing the various constants and concentrations as negative logarithms, Langelier's equation is:

$$pH_s = pK_2' - pK_s' + pCa + pAlk. \tag{23}$$

where K_2' is the second ionization constant for carbonic acid and K_s' is the solubility product constant, both corrected for the effect of the ionic strength or total dissolved salts and the temperature. Larson and Buswell[14] proposed a salinity term for the correction for ionic strength. Expressing concentrations as mg/l and using the logarithmic form, their equation is:

$$pH_s = \log\frac{K_s}{K_2} - \log Ca^{++} - \log Alk. + 9.30 + \frac{2.5\sqrt{\mu}}{1 + 5.3\sqrt{\mu} + 5.5\,\mu} \tag{24}$$

where, for waters with a mineral content of less than 500 mg/l, $\mu =$ 0.000025 times the total mineral content.

Langelier proposed naming the difference between the observed pH of a sample of the water and its calculated pH_s the calcium carbonate saturation index (S.I.). A plus value for $pH_{actual} - pH_s$ indicates a lack of excess CO_2 and hence calcium carbonate scale-forming qualities, while a minus value for this difference indicates an excess of CO_2 or scale-dissolving qualities.

It has been shown[15,16] that with a water with a high pH_s value, such as a lime–soda ash–softened water, the numerical value for the saturation index indicates a very much smaller excess or deficiency of carbon dioxide and, hence, a much lower tendency to dissolve or deposit calcium carbonate scale than does the same numerical value for the S.I. for a low pH_s water. Because, in this respect, the S.I. is not quantitative, but shows only the directional tendency, other indexes and methods of evaluating the scale-forming or -dissolving properties of a water have been developed.

Ryznar's Stability Index

An index was proposed by Ryznar,[15] using the empirical expression $2pH_s - pH$, which he called the stability index to differentiate it from the saturation index. Values of the stability index greater than about 7.0 indicate a corrosive water, while values less than 7.0 indicate a scale-forming water. This index is of particular interest in evaluating waters of widely different composition, but in any one plant if the saturation index and stability index are plotted daily on the same scale, one plot is simply the invert of the other and has the same significance. The stability index does seem to have a particular value in predicting the performance of a water when heated in hot-water heaters and coils.

The Momentary Excess (M.E.)

The momentary excess (M.E.) was proposed by Dye[17] as a quantitative measure of the theoretical degree of supersaturation of a water with respect to calcium carbonate. It is based on the equation for the solubility product constant [Eq. (19)] modified to read:

$$(\mathrm{Ca}^{++} - x) \times (\mathrm{CO}_3^{--} - x) = K_s' \qquad (25)$$

where Ca^{++} and CO_3^{--} represent mols of calcium and carbonate ions before precipitation and x represents mols of calcium carbonate that must precipitate to establish equilibrium. K_s' is the solubility product constant for calcium carbonate, corrected for ionic strength and temperature. Converting to familiar terms and solving for x, this becomes:

$$(\mathrm{Ca}^{++} \times \mathrm{CO}_3^{--}) - (K_s' \times 10^{10}) - x(\mathrm{Ca}^{++} + \mathrm{CO}_3^{--}) = -x^2 \qquad (26)$$

where Ca^{++} is the calcium hardness of the water as determined by an EDTA titration and CO_3^{--} is the carbonate-ion concentration as determined by the nomograph on evaluation of carbonate alkalinity in *Standard Methods.*[18] A nomograph for solving Eq. (26) was presented.[17]

The Driving-force Index (D.F.I.)

McCauley's driving-force index (D.F.I.)[19] was devised to express the driving force tending to cause calcium carbonate deposition if the levels of calcium hardness and carbonate alkalinity are markedly different. He defined it as follows: "The DFI is an exact measure of the tendency to deposit calcium carbonate, being a statement of the law of mass action which defines all precipitations." The equation for the D.F.I. is:

$$\text{D.F.I.} = \frac{\mathrm{Ca}^{++} \times \mathrm{CO}_3^{--}}{K_s' \times 10^{10}} \qquad (27)$$

where Ca^{++} and CO_3^{--} represent concentrations in mg/l, as $\mathrm{CaCO_3}$, and K_s' is the solubility product constant for $\mathrm{CaCO_3}$, corrected for ionic strength.

The Marble Test[20]

The marble test is a rapid method of determining if a water is in balance with solid calcium carbonate. The test procedure is given in detail in the AWWA publication "Simplified Procedures for Water Examination." Essentially, the test consists of determining the alkalinity on one portion of the sample being tested and adding an excess of finely powdered calcium carbonate to another portion of the same sample in a 300-ml glass-stoppered BOD bottle. This sample is mixed by shaking at frequent intervals for at least 3 hr, settled overnight, and filtered. The alkalinity is then determined on the filtered sample. If the alkalinity has increased, it indicates that the water was not saturated with calcium carbonate and could not deposit any protective scale. In fact it might dissolve any previously deposited scale and would then be corrosive. If the alkalinity has decreased, the water is supersaturated with calcium carbonate and may deposit protective scale or maintain a coating already deposited. If the alkalinities are the same, the water is stable. It should not dissolve any previously deposited protective scale, but neither will it maintain or improve such a coating.

Enslow's Stability Indicator

Enslow's stability indicator is simply a device for a continuous-flow marble test. It consists of a bed of fine calcium carbonate contained in a 1- or 2-l leveling bulb or pear-shaped separatory funnel and two glass tubes 2 in. in diam and 18 in. long and containing 6-in.-deep beds of crushed marble which has been screened to pass a 14-mesh sieve and be retained on a 30-mesh sieve. The crushed marble is supported by a 6-in. bed of ¼- to ⅛-in. silica gravel. The water to be tested is passed continuously upward through the fine calcium carbonate in the separatory funnel and then downward through the two crushed-marble filters in series. It is best to use a constant-level tank or bottle as the source of water and to place an air trap in the tubing between this and the bottom of the separatory funnel. The two crushed-marble filters are placed side by side, and suitable tubing leads from the top of the separatory funnel to the top of the first filter and from the bottom of the first filter to the top of the second filter. The bottom outlet of the second filter is connected by rubber tubing to the inlet tube in a 250-ml receiving bottle or flask fitted with a two-hole rubber stopper containing the inlet and outlet tubes. The inlet tube extends nearly to the bottom of the flask, while the outlet tube extends only to the bottom of the stopper and is connected to a glass tube drawn out to form a dropping tube. The flow rate is adjusted to about 80 to 100 drops per minute through the apparatus. With the installation of some two-way and three-way glass stopcocks, the filters may be backwashed to remove accumulated fine calcium carbonate and any adsorbed air.

In practice, the receiving flask is removed and replaced with a clean flask whenever routine samples are taken for control testing. The average alkalinities for the day's operation may then be used to determine the scale-forming or -dissolving character of the water.

The various indexes and laboratory methods described above constitute the several means available to the operator for predicting the performance of a water softened by the lime or lime–soda ash method in the distribution system. Many recommendations can be found in the literature for the composition of a mildly scale-forming lime-softened water which will give protection against corrosion.[19,21–25] There can be no hard limits for pH, alkalinity, calcium, magnesium, or the various indexes and test results. It is true that the lower limit for alkalinity is usually set at 35 mg/l and for calcium at 40 to 45 mg/l, but the upper limits may be quite variable and are dictated by the composition of the water being softened, the treatment used, and the performance of the water in the mains.

As a rule, waters with a high pH_s, such as lime-softened waters, require a saturation index of 0.8 to 1.0 or even higher to have definitely scale-forming properties. Momentary excess (M.E.) values of 6.0 or 7.0 to 15.0 coupled with driving force index (D.F.I.) values of approximately the same range will result. The stability indexes will usually indicate that little difficulty will be experienced with this water when heated in a domestic water heater. The scale-forming tendency may be retarded, if necessary, by the application of 0.25 to 0.50 mg/l of a polyphosphate.

Generally, with the same saturation index, a high-alkalinity–high-calcium water softened by the lime–soda ash method will give more protection than a low-alkalinity–low-calcium water. Also, a high-alkalinity–low-calcium water will give more protection than a low-alkalinity–high-calcium water. As shown in Table 9-1, this is true at high as well as at low temperatures. In this table four waters of various hypothetical compositions are considered. Water 1 might be typical of the effluent from a plant using selective calcium carbonate softening of a hard, but low-magnesium water. Water 2 represents the effluent from a plant treating high-magnesium waters with noncarbonate hardnesses of 50 mg/l or more where a low alkalinity may mean a saving in soda-ash consumption. Water 3 is also the result of treating a high-magnesium water but with a low noncarbonate hardness where alkalinity reduction is not so important. Water 4 would represent the effluent from a plant softening a low-magnesium water with a noncarbonate hardness of 50 mg/l or more.

The saturation index assumed in all four cases is +1.0 at 15 °C. It can be seen that a uniform saturation index of +1.0 does not mean that they will all have the same degree of supersaturation with respect to calcium carbonate as indicated by the M.E. values, nor will they all have the tendency to deposit calcium carbonate scale, as indicated by the D.F.I. values. Increasing the temperature to 75 °C (167 °F) decreases the pH_s values by about 1.0 pH unit, but the actual pH value would be decreased by a like amount so that the saturation index remains almost constant. Dye's method[16] was used for calculating the change in pH values at the higher temperatures. The degree of supersaturation becomes much less for all four waters as they are heated, but it would be expected that the excess would be deposited a little more rapidly when heated because of the increase in D.F.I. values. In actual practice it has been found that the high-carbonate alkalinity such as in waters 1 and 3 gives the most protection.[25]

TABLE 9-1 Comparison of Four Hypothetical Waters Softened by the Lime–Soda Ash Method

Hypothetical composition	1	2	3	4
Calcium hardness	75	45	45	75
Magnesium hardness	10	40	40	10
Total hardness	85	85	85	85
Alkalinity	60	35	60	35
Total solids	200	200	200	200
Characteristics at 15 °C				
pH$_s$ at 15 °C	8.39	8.85	8.61	8.61
pH at 15 °C	9.39	9.85	9.61	9.61
OH$^-$	0.61	1.72	1.00	1.00
S.I. at 15 °C	+1.00	+1.00	+1.00	+1.00
M.E. at 15 °C	10.6	8.9	12.7	7.9
D.F.I. at 15 °C	10.1	5.3	7.1	7.0
Characteristics at 75 °C				
pH$_s$ at 75 °C	7.40	7.85	7.61	7.61
pH at 75 °C	8.54	8.79	8.76	8.69
OH$^-$	3.9	7.0	6.6	5.5
S.I. at 75 °C	+1.14	+0.94	+1.15	+1.08
M.E. at 75 °C	3.3	4.8	4.8	2.3
D.F.I. at 75 °C	12.6	6.6	11.4	2.4

Hardnesses, alkalinity, OH$^-$, and M.E. values expressed as mg/l CaCO$_3$.

The four hypothetical compositions shown in Table 9-1 do not, of course, represent the entire range of compositions possible in waters softened by the use of lime or lime–soda ash. In many plants, because of cost, soda ash is not used even though the amount of noncarbonate hardness in raw water indicates that its use would be desirable. Plant effluent hardnesses of 110 to 120 mg/l are not uncommon for these partially softened waters. If the water has received complete treatment with lime, all the noncarbonate hardness remaining is in the form of calcium compounds, and, consequently, most of the hardness is made up of calcium hardness. Such waters may be quite troublesome in the mains unless properly stabilized because of the soft, nonprotective scale which they deposit. Some experimenting may be necessary to determine the optimum saturation index, M.E., and D.F.I. values which will give the best protection.

Magnesium Hydroxide Stabilization in Lime-softened Waters

The stabilization of a water softened by the lime–soda ash method with respect to calcium carbonate is only a part of the problem facing the operators of plants using this treatment. In some cities using lime-softened water, deposits of magnesium hydroxide (brucite) together with varying amounts of adsorbed silica have been found in hot-water heaters, especially those operated at temperatures above 160°F.[26] Examination of samples by polarizing microscope and x-ray indicate that magnesium silicates analogous to the natural silicate, serpentine, are present in these deposits.[27] Generally these deposits only occur when the water is heated, and given a sufficiently high initial magnesium concentration and pH value, the higher the temperature the more quickly the deposits form and, in the presence of silica, the more silica is adsorbed.

The pH of a lime–soda ash softening plant effluent is dependent upon its pH_s, the saturation index, M.E., and D.F.I. values desired. The solubility of magnesium hydroxide decreases with an increase in temperature, as is shown by the decrease in the solubility product constant $K_{Mg(OH)_2}$ from about 2.21×10^{11} at 15° C to about 0.513×10^{-11} at 75° C. These values were obtained (with no correction for ionic strength) by the interpolation in the table from Travers and Nouvel, as given in a paper by Ryznar, Green, and Winterstein.[28] As can be seen from the examples in Table 9-1, the pH values for most waters softened by the lime–soda ash method will decrease by approximately 1.0 pH unit as the temperature is increased from 15 to 75° C. However, since K_w increases from about 0.45×10^{-14} at 15° C to about $20.34 \times {}^{-14}$ at 75° C, the net result is a sharp increase in hydroxyl ion concentration as can be seen in this table, and if the solubility product constant $K_{Mg(OH)_2}$ is exceeded at this elevated temperature, magnesium hydroxide will precipitate.

As pointed out by Larson,[1] equilibrium conditions with respect to magnesium hydroxide are almost never attained, so that with either split treatment or the excess-lime and recarbonation methods the primary basin effluent is usually supersaturated with magnesium hydroxide. Recarbonation or the addition of bypassed raw water neutralizes this hydroxide alkalinity, converting it to carbonate and bicarbonate alkalinity. At present, it is commonly accepted that a maximum of 40 mg/l of magnesium hardness in the plant effluent will cause little trouble with scale in hot-water heaters operating at the normal temperature of 140° F if the pH value is 10.0 or below.

Table 9-2 shows the maximum allowable amount of magnesium hardness in lime-softened water which will not precipitate in 140° F domestic hot-water heaters. The table is based on experimental work done by the St. Louis County Water Company, using lime-softened Meramec River water.[29]

With the excess-lime and recarbonation method, the reduction of magnesium hardness to less than 40 mg/l is only a matter of using enough lime. As shown in Fig. 3, in one plant a hydroxide alkalinity of 54 to 60 mg/l will reduce the magnesium hardness to 40 mg/l or less. This is an excess hydroxide alkalinity of 14 to 32 mg/l or an excess of 73 to 166 lb of 90% lime per million gallons. Where split treatment is used, the problem is one

TABLE 9–2 Approximate Amounts of Maximum Allowable Magnesium Hardness in Lime-softened Water Which Will Not Precipitate at 140° F in Domestic Hot-water Heaters

pH of Water at 25 °C	Magnesium (as $CaCO_3$), mg/l
9.0	65
9.2	57
9.4	51
9.6	45
9.8	40

of bypassing the minimum amount of raw water required for the neutralization of the hydroxide alkalinity in the primary basin effluent and providing the desired amount of bicarbonate alkalinity. The percentage of raw water bypassed must be kept as low as possible in order that the magnesium reintroduced in the bypassed water is at a minimum. It may even be necessary to set the desired bicarbonate alkalinity at zero in Eq. (14) to reduce the per cent bypass and then after filtration recarbonate to the desired pH.

In the early days of lime–soda ash softening there were no rapid procedures for calcium and magnesium determination, and even the soap method for the estimation of total hardness was slow and often inaccurate. The determinations of soap hardness and total and phenolphthalein alkalinities were the only control tests possible. The full import of excess hydroxide alkalinity in the reduction of magnesium was not recognized until Hoover proposed the excess-lime and recarbonation method in the late 1930s. However, control titrations were still lacking until the E.D.T.A. methods for titrating for total and calcium hardnesses were developed. These methods were widely publicized in 1950, presented as tentative methods in the tenth edition of *Standard Methods for the Examination of Water, Sewage, and Industrial Wastes* and made standard in the eleventh edition.

In the hands of an experienced operator these methods for determining the total and calcium hardnesses and then the magnesium hardness by difference are, for all practical purposes, as reliable as the older gravimetric procedures for determining calcium and magnesium. These methods should therefore be added to the list of control tests to be used to check the process of softening at various stages in the plant.

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10

Ion-exchange Softening

By EUGENE BOWERS

CATION-EXCHANGE SOFTENING

Historical

Water softening by the cation-exchange process depends upon the ability of certain insoluble substances to exchange cations with other cations dissolved in water. When a hard water is passed through a sodium cation exchanger, the calcium and magnesium in the hard water are replaced by sodium from the exchanger; and because the reaction is reversible, after all of the readily replaceable sodium has been exchanged for calcium and magnesium from the hard water, the "exhausted" cation exchanger can be regenerated with a solution of sodium chloride (common salt). In the regeneration process, the calcium and magnesium of the exhausted cation exchanger are replaced with a fresh supply of sodium from the regenerating brine solution. Then, after a washing with water to free it from brine, the regenerated exchanger is ready to soften a fresh supply of hard water.

The use of ion exchange by man in his struggle for existence and betterment is as old as civilization itself. In recording his history, mankind has many times indicated observations which had as their basis the ion-exchange process. An appreciation of the phenomenon was slow in developing. For the lack of scientific knowledge, his superstitions and preconceived notions led to wrong concepts. For years the knowledge of those who went before did much to mold the thoughts of those to follow. It was not until rather recent history that the fundamental chemical laws of ion exchange were investigated and understood.

One of the first records we have in which man began to think about such phenomena is given in the writings of Lord Francis Bacon. In 1623, writing in *The New Atlantis,* Bacon describes certain imaginary pools: "And we also have pools of which some do strain water out of salt and others do turn fresh water into salt." Later in *Sylva Sylvarum,* he gave a method for obtaining fresh water from the sea. He says that if one digs a hole on the seashore at a point ". . . somewhat higher than high water and as deep as low water mark, when the tide cometh in [this hole] will be filled with water fresh and potable." He did not take credit for discovery of this fact but says that it was used "on the Coast of Barbary." He knew from experience that this purification power of the soil would not go on indefinitely for he goes on to say ". . . that trial hath been made of salt water passed through earth through ten vessels, one within another, and yet it hath not lost its saltiness as to become potable; but when drayned through twenty vessels hath become fresh." Thus the purifying effect of soil was known to be limited.

It was almost two centuries after Bacon's writings that studies on the adsorption of components of manure liquors onto soils were made by Sir Humphrey Davy, Huxtable, and others.[1] In 1833 Fuchs[2] reported that when certain clays were treated with lime they released potassium and sodium. However, it was H. S. Thompson who is credited with recognizing the ion-exchange phenomenon.[3] He reported in 1845 that in the passage of a liquid containing ammonium through soil, the ammonia was absorbed, and subsequent treatment of the soil with lime released the ammonia.

J. Thomas Way[4] continued the studies of Thompson during the years 1850 to 1854. Further investigations led him to report, in part, the following observations and conclusions to the Royal Agricultural Society of London:

1. The exchange of calcium and ammonia ions in soils noted by Thompson was verified.
2. Base-exchange substances were silicates, and of the silicates only those which were hydrated displayed any base-exchange properties.
3. Heating soil samples destroyed the base-exchange properties.
4. Base-exchange materials could be synthesized from soluble silicates and alum. Thus the silicates of aluminum were responsible for the exchange of ions.
5. Exchange of ions is not due to physical adsorption.

6. Some ions are removed more easily than others.
7. Ions are exchanged by equivalent amounts in the soil.

The reversibility of the base-exchange reaction was not appreciated by Way; in fact, he believed that there was a preferential order for the replacement of bases, but that this replacement was not reversible. This error was corrected a few years later by Eichborn,[5] and it is to the investigations of Way and Eichborn that we are indebted for the essential theory on which ion-exchange water softening is based.

The first real attempt to utilize ion-exchange materials industrially was in the beet sugar industry,[6–8] in just the reverse of the manner in which they are used in water softening. The process apparently never achieved commercial success.

The application of ion exchangers to water purification did not receive attention until the first decade of the twentieth century. There was some little discussion between Rümpler[8] and Gans[9] over credit for the suggestion. It is fairly certain, however, that Gans and his organization made the first usable synthetic materials that were actually employed for the purpose on a practical scale, and in 1906 he obtained a German process patent for the softening of water by means of base exchange.[10]

Gans' cation exchangers, made by the fusion of appropriate raw materials, were generally satisfactory according to the only standards then prevailing. These were, however, quite slow in their rate of exchange, in consequence of which it was standard practice to require a softening period of 8 to 12 hr and a regeneration period of similar duration.

A few years after water softening with the Gans synthetic materials was introduced into the United States, a bentonitic clay that possessed marked base-exchange properties was found. This clay, after processing, yielded a satisfactory softening material, but it too was limited by a relatively slow softening and regeneration period.

The next development in ion-exchange water-softening materials was the introduction of naturally occurring New Jersey greensand, or glauconite, as the softening medium.[11] With greensand the rate of exchange was so rapid that high softening rates and short periods of regeneration made it possible to use the process effectively in industry. And almost simultaneously another type of inorganic cation exchanger was introduced. It was prepared as a gelatinous precipitate under carefully controlled conditions. The precipitate was filter pressed and otherwise treated before final drying.[12]

It was not long until the synthetic siliceous "gel"-type exchangers completely replaced the precipitate exchangers. In these exchangers the solution components are brought together under such conditions that no precipitate forms. After mixing, the whole mass sets to a stiff gel embracing all the constituent elements of the reacting solutions. The gels are dried, crushed, and screened to the proper size without additional processing.[13]

The limitations of the siliceous ion exchangers became more evident as the ion-exchange process was studied and expanded. Waters low in silica content had a tendency to dissolve out the silica structure of the material with a resulting drop in capacity and in some cases a collapse of the particle structure.[14] The potential of ion-exchange softening had increased to the point where a great deal of research time and money were spent in trying to increase both the exchange rate and the exchange capacity of the gel-type ion exchangers. The resulting increase in exchange capacity did not offset the growing desire for an improvement in water quality which could be brought about by the exchange of ions other than calcium and magnesium for sodium. An entirely new field was opened with the discovery of sulfonated coal cation exchangers, which, when regenerated with mineral acids, would exchange hydrogen for all ionized cations in the water. About this same time the Englishmen Adams and Holmes were demonstrating that certain synthetic organic resins could be made to exchange ions.[15] Starting with the year 1935 they were granted a number of patents for stable, high-capacity sulfonated phenolic resins.[16]

With the development of sulfonated coal and the synthetic phenolic resins the potential of these new materials was quickly recognized, and research into water treatment took on renewed importance. D'Alelio,[17] in the United States, was granted a patent in 1945 for a new, extremely stable synthetic cation-exchange resin derived from sulfonating polymerized styrene. To keep pace with the cation exchangers, anion exchangers were being developed which opened an entirely new field of water treatment. Not only could softening be effected, but "distilled water" could be produced by passing the mineralized water through beds of cation and anion exchangers to completely remove all cations and anions. With knowledge of the basic structure of the ion exchangers and control over the complete synthesis process, by 1955 it became possible to produce "tailor-made" exchangers to suit almost any problem dealing with ion exchange in aqueous solutions.

Sodium Cation Exchangers

The use of the term "zeolite" has been loosely applied to all those materials which are used for water softening. They have included greensand, bentonitic clay, synthetic gel-type mineral, sulfonated coal, and the synthetic organic resins. Strictly speaking, the term should include only those inorganic aluminosilicates which display ion-exchange properties. Zeolite comes from two Greek words (*zein* and *lithos*) which mean "boiling stone." This term was first applied by Cronstedt,[18] the Swedish geologist, in 1756 to a class of minerals which expanded and gave off their water of hydration when heated. Today the exchangers can be classified into two types: the naturally occurring and manufactured inorganic mineral zeolites and the synthetic organic resins. The zeolites have a rated capacity for hardness removal of 2,800 grains per cubic foot for the naturally occurring minerals to a capacity of 14,000 grains per cubic foot for the synthetic zeolites. Synthetic resins have rated capacities ranging up to a high of 35,000 grains per cubic foot.

The early precipitate-type zeolites used in water softening have only historical interest and will not be included here. Interesting accounts of the history of these materials have been recorded and the reader is directed to some of the references.[12,19]

Natural greensand (glauconite) is found in various parts of the world, but the largest principal commercial deposit is in New Jersey. The mineral is open-pit mined, washed, screened, and treated with caustic to remove clay. Further treatment with alum, silicates, and other salts produces a durable greenish-black mineral which is relatively inert except for the ion-exchange properties. It has an exchange capacity of 2,800 grains per cubic foot when regenerated at a level of 0.45 lb of salt per kilograin of hardness removed from the treated water. The porosity can be increased by additional chemical treatment with a resulting exchange capacity of 3,500 to 5,000 grains per cubic foot. The gain in capacity is offset by the production of a more friable material whose life is greatly reduced by the mechanical and chemical attrition which takes place during operation. The normal capacity mineral is rugged and stands up well in operation without particle breakdown. Chemically it is resistant over a pH range of 7.2 to 8.0. Below this pH range it is dissolved, and above, it softens and then breaks down. It is not affected by chlorine and will give satisfactory service up to a temperature of 110 °F. One good feature of the greensand is that ferrous and manganous ions are removed during softening. Powell[20] states that, "Ten parts per million of soluble iron will be removed for each 342 ppm of hardness." The optimum operating flow rate is 3 to 4 gpm per square foot of top surface area for a bed 24 in. deep.

Synthetic siliceous gel-type zeolites are prepared by the mixing and reacting together of solutions of sodium silicate and sodium aluminate under such conditions that no precipitate forms. The whole reaction mass is poured into a shallow vat where it sets to a homogeneous gel which contains all the constituent elements of the solutions. The gel is dried, crushed, and screened to a particle size of 0.3 to 0.5 mm without intermediate processing.[13] It has a weight of 50 lb per cubic foot. The synthetic zeolites have exchange capacities in the range of 8 to 14 kilograins per cubic foot when regenerated with 0.4 to 0.5 lb of salt per kilograin of hardness removed. The exchange capacity appears to be dependent upon the SiO_2:Al_2O_3 ratio. Mattson[21] found that the exchange capacity of a zeolite increases as the $SiO_2:Al_2O_3$ ratio increases to about 6:1. The capacity decreases gradually as the ratio is increased beyond this point. Generally $SiO_2:Al_2O_3$ ratio of gel-type zeolites is within the range of 3:1 to 7:1. However, such factors as quality of water being softened, porosity, and particle size do much to determine the operating capacity and life of the material.

Flow rates of 3 to 4 gpm per square foot may be used. Under certain conditions of good water quality this rate may be increased to 6 gpm per square foot. Siliceous zeolites maintain their best stability in the pH range of 6.8 to 8.3. Water temperatures should not exceed 90 °F, and chlorine will not affect them adversely. They will not tolerate the quantity of iron that greensand will without serious loss of capacity. Streicher et al.[14] indicate that the economic operating lives of the zeolites are materially reduced by waters low in silica. Several revivification methods used on "worn-out" siliceous zeolites proved to be relatively ineffective. The silica content of water passing through the siliceous zeolites will increase due to the slow dissolution of the mineral.

In about 1935 it was discovered that a wide variety of particulate organic materials could be made to exchange ions after they were sulfonated. In sulfonation, ion-exchangeable sulfonate ($-HSO_3$) groups are fixed to the material by treatment with sulfuric acid, sulfur dioxide, or chlorosulfonic acid. From 1935 to the present time patents have been issued almost continually for making ion exchangers from all types of natural (e.g., coal, lignite, and peat fibers) and synthetic organic materials. The first commercial grades of sulfonated exchangers were made from bituminous coal. After processing, this stable product would not only exchange sodium for calcium and magnesium, but when regenerated with mineral acid would exchange hydrogen ions for all cations in solution. Thus, a new technique for radically changing water quality became available to the water-treatment industry.

Operating in the sodium softening cycle, sulfonated coal has an exchange capacity of 8,000 grains per cubic foot when regenerated with 0.45 lb of salt per kilograin of hardness removed. Sodium content and hardness of the water to be softened do much to influence the exchange capacity. Exchange rates are rapid, so that the operating flow rates may be in the range of 4 to 6 gpm per square foot. The pH of the influent water may vary from 2 to 10; even a higher pH can be tolerated if the water is stable so that calcium carbonate will not be precipitated on the particles. One disadvantage of the sulfonated coals is their vulnerability to oxidation by chlorine with resulting "color throw" and particle breakdown. Reaction rates between chlorine and sulfonated coal are so rapid that chlorine cannot penetrate more than the top several inches of the bed. Several investigators[22–24] found that as the chlorine is depleted at the top of the bed, the rest of the bed can become contaminated by bacteria. Contamination is introduced in the regeneration cycle by unsterile brine. To maintain particle stability and good operating characteristics, it was necessary to soften only unchlorinated water. Sterile conditions were maintained in the bed by the introduction of formaldehyde during the brining. Subsequent rinsing eliminated all traces of the formaldehyde. As the high-capacity synthetic resins were developed, the sulfonated coals and natural and synthetic zeolites soon dropped from the commercial market.

About the same time sulfonated coals were being developed, Adams and Holmes in England were demonstrating the ability of synthetic organic resins to exchange ions. The resins, like all to follow, were copolymers of organic compounds such as phenols, aldehydes, and styrene and vinyl derivatives. Familiar examples are the plastics Bakelite, a phenol-formaldehyde resin, and polystyrene, a styrene-divinylbenzene polymerization product. In the polymerization process several low-viscosity, volatile liquids are reacted in fixed ratios. As the reaction proceeds, the volatile liquids are linked together to form long chain products which in turn cross link with other chains to produce a stable insoluble solid "electrolyte." In certain resins the ion-exchangeable groups are present in the raw material, and the completed resin requires no additional processing, while others require intermediate processing to fix the ion-active groups to the solid particles. Synthetic ion-exchange resins are identified by the base material—phenolic, polystyrene, etc.—and by the active groups— $-HSO_3$, $-COOH$, $-OH$, etc. Current resin production is in the form of spherical particles or "beads" in the effective size range of 0.40 to 0.50 mm. Within the normal softening confines particle size does not affect the operating exchange capacity; only backwash and head loss characteristics are influenced.

Phenolic resins are produced by the condensation of *m*-phenolsulfonic acid with formaldehyde. The ion properties of the *m*-phenolsulfonic acid are about the same after polymerization as before, only the mobility of the anionic $-HSO_3$ ion active groups has been slightly reduced. Nachod[25] states that "The final product contains 50–70% solids as a 'solution' of a high molecular weight sulfonic acid in water."

Exchange capacity of the phenolic resin is 12,500 grains per cubic foot at a salt consumption of 0.45 lb of salt per kilograin of hardness removed. Like the sulfonated coals the phenolic resins are subject to degradation by chlorine, resulting in complete dechlorination of ~~the process stream within~~ the top few inches of the bed. The action of the chlorine causes "color throw" and subsequent loss of material in the backwashing cycle. Although the organic base of the resin will not support bacterial growth, it does provide a good environment for their growth.[22] After several years of testing, operating units of the phenolic resin were found to be almost devoid of exchange capacity. Examination of the beds found that below the top few inches the resin particles were slimy and cemented together so that an opening of less than 2 in. existed down through the unit. After the resin was mechanically broken up and sterilized with formaldehyde, the capacity returned to near normal.[23,24] Weekly sterilization, in which formaldehyde was combined with the brine, maintained the unit in good operating condition. Commercially the phenolic resins are used for special purposes only. One of its shortcomings is turned to an advantage. It is an effective dechlorination agent where chlorine must be removed from the water.

Practically all the present-day exchangers used in softening are the polystyrene ion-exchange resins which are produced by polymerization of styrene monomer with divinylbenzene (DVB).[17] Stability and mechanical strength of the resin particles depend on the degree of cross linkage which is developed in the polymerization process and are dependent upon the amount of DVB used in the process. This is expressed as per cent of DVB used and is normally synonymous to per cent cross linking. Density, durability, and exchange capacity are affected by the amount of cross linkage. Current production is in the 8 to 12 per cent range. However, 8 per cent appears to be that most commonly used for water softening. After the basic resin particle has been produced, the polymer is sulfonated with sulfuric acid and other reagents to produce the anionic exchange groups $-HSO_3$. The resins appear to be "solid solutions," in that the exchange capacity is greater than can be explained on a surface area basis. Kunin and Myers[26] state: "The various cation and anion exchange resins may be considered as insoluble, high molecular weight polymeric electrolytes." For further technical discussion the reader is directed to several references.[27–29]

Exchange capacity of the polystyrene resins is 28,000 grains per cubic foot when regenerated with 0.45 lb of salt per kilograin of hardness removed. As in all ion-exchange operations, the operating exchange value will be affected by the hardness and concentration of sodium ions in the influent water. The polystyrene resins will tolerate chlorine and pass it through the bed without change; thus the material can be kept sterile and free of bacteria. The resins operate well over a pH range of 0 to 14 and will tolerate temperatures up to 250 °F. Operating characteristics of these resins will be explored more thoroughly when the operating procedures are discussed.

The relative exchange capacities of the various ion exchangers are shown in Table 10-1. All the data were taken from manufacturers' data and are calculated to the same salt efficiency. An increase or decrease in the regenerant dosage will increase or decrease the capacity with varying effects on the efficiency of the operation.

Most of the popular advertising has been directed to the fact that the

TABLE 10–1 Relative Exchange Capacity of Cation Exchangers

Cation exchanger	Capacity, kgr/cu ft	Regenerant, lb NaCl/ cu ft	Efficiency, lb NaCl/ kgr removed
Greensand	2.8	1.26	0.45
Processed greensand	5.5	2.47	0.45
Synthetic siliceous zeolite	11.0	4.95	0.45
Sulfonated coal	8.2	3.69	0.45
Resin, phenolic	12.5	5.63	0.45
Resin, polystyrene	28.0	12.6	0.45

domestic consumer will reap great rewards from softened water. These benefits are based on the lower costs of soap used for his cleaning, longer life for plumbing, better taste in cooked foods, and the "extra" luxury of bathing in "mountains" of suds.[30–32] The problem is no less important to the industrial and commercial user. Process water must be softened for many industries to give the right "feel" to finished cloth, produce clearer pictures, and reduce precipitation of sludges in boilers and heating pipes, just to mention a few. In fact, the need for high water quality has reached a point where processing beyond softening has become commonplace. The vast use of synthetic detergents has not reduced the need for softened water.[33,34] The advantages of softened water in the home and industry have become so well established through use and the development of easily operated equipment that softening is not only commonplace but expected.

In the ion-exchange softening reaction the sodium concentration of the water increases. This may be a problem when this water is used on some plants and soils or if it is used by people requiring a low sodium diet.

Patent Problems

The early development of the cation-exchange softening process was complicated and retarded by almost continuous patent litigation. There was never a United States patent issued covering so broadly the cation-exchange softening of water such as was taken out by Gans in Germany in 1906.[10] The litigation referred to was concerned almost entirely with an apparatus patent by Gans[35] which was construed in several courts to cover the most usual types of exchange-softening apparatus, while other courts took the opposite view. The patent itself expired in August, 1933. Although a large number of patents have been issued recently on the manufacture of ion-exchange materials, and especially the resins, there appears to have been a concerted effort to push the process forward through licensing of patents rather than try to hold exclusive manufacturing rights.

ION-EXCHANGE SOFTENING

Three methods may be used for water softening by ion exchange. They are: sodium cycle, split stream, and demineralization. Only sodium cycle will be given major attention in this chapter; split stream will be outlined, and demineralization of water by ion-exchange techniques can be found in several papers.[25–29] The major thrust in softening is in the use of sodium cycle operation. Softening of water by ion exchange consists ~~essentially~~ of passing hard water through a bed of ion exchanger. There the hardness components of the water, calcium and magnesium ions, are removed from solution and replaced in solution by sodium. In practice the exchange rate is so rapid that almost any water can be easily and completely softened at normal flow rates regardless of hardness.

It is easy to indicate by chemical equations the reactions which occur in cation-exchange water softening and in regeneration. The exact mechanism of the reaction, however, is not clearly understood. Whatever the final explanation of the cation-exchange reaction may be, it is evident that its successful completion is dependent upon securing adequate contact of the water with the exchange material. Other conditions being equal, adequate contact is probably the most important requisite in successful cation-exchange water softening; and to secure this contact requires experienced correlation of all such important influencing factors as hardness of water, depth of material, rate of flow, and character of the exchanger. Thus, it follows that, if continued maximum contact is to be secured, reasonably clear water must be applied to the exchanger to avoid coating of its particles with colloidal or suspended matter from the water.

The following schematic equations, in which R represents the anionic component of the ion exchanger, indicate the reactions which take place in cation-exchange softening:

$$\mathrm{Ca(HCO_3)_2} + \mathrm{Na_2}R \rightarrow \mathrm{Ca}R + 2\mathrm{NaHCO_3}$$

$$\mathrm{Mg(HCO_3)_2} + \mathrm{Na_2}R \rightarrow \mathrm{Mg}R + 2\mathrm{NaHCO_3}$$

Carbonate hardness **Soluble nonhardness**

$$\mathrm{CaSO_4} + \mathrm{Na_2}R \rightarrow \mathrm{Ca}R + \mathrm{Na_2SO_4}$$

$$\mathrm{CaCl_2} + \mathrm{Na_2}R \rightarrow \mathrm{Ca}R + 2\mathrm{NaCl}$$

$$\mathrm{MgSO_4} + \mathrm{Na_2}R \rightarrow \mathrm{Mg}R + \mathrm{Na_2SO_4}$$

$$\mathrm{MgCl_2} + \mathrm{Na_2}R \rightarrow \mathrm{Mg}R + 2\mathrm{NaCl}$$

Noncarbonate hardness **Soluble nonhardness**

And when the exhausted exchanger is regenerated, essentially the reverse action takes place:

$$\mathrm{Ca}R + 2\mathrm{NaCl} \rightarrow \mathrm{CaCl_2} + \mathrm{Na_2}R$$
$$\mathrm{Mg}R + 2\mathrm{NaCl} \rightarrow \mathrm{MgCl_2} + \mathrm{Na_2}R$$

These equations emphasize the base-exchange nature of cation-exchange softening, indicating that the only change in the composition of the water is the replacement of the hardness-producing bases—calcium and magnesium—by sodium, which does not produce hardness. In this respect it is worth noting that the softening reaction may usually be carried to such a degree of completion that no calcium or magnesium can be found in the softened water by ordinary analytical methods; in other words, with the majority of waters, a properly designed and operated cation-exchange softener is capable of delivering water with a hardness that is actually zero, even though, in industrial and municipal practice, the term "zero hardness" may actually mean only "insignificant hardness."

In addition to the hardness in the water, relatively small amounts of iron and manganese may be present in the bivalent form in waters high in bicarbonate. Both of these ions will be removed from solution during softening. A resin unit that is exhausted for softening will continue to remove these troublesome ions from the water.

Trace amounts of aluminum, which may remain in solution from pretreatment with alum, will also be removed. The reactions are:

$$\mathrm{Fe(HCO_3)_2} + \mathrm{Na_2}R \rightarrow \mathrm{Fe}R + 2\mathrm{NaHCO_3}$$
$$\mathrm{Mn(HCO_3)_2} + \mathrm{Na_2}R \rightarrow \mathrm{Mn}R + 2\mathrm{NaHCO_3}$$
$$\mathrm{Al_2(SO_4)_3} + 3\mathrm{Na_2}R \rightarrow \mathrm{Al_2}R_3 + 3\mathrm{Na_2SO_4}$$

Only to a slight degree will the iron, manganese, and aluminum be removed from the exchanger during regeneration with salt brine. Since these ions will readily form insoluble hydroxides on a shift in pH, a large percentage of the exchanged ions will precipitate within the ion-exchange particle and become mechanically locked within the structure. Experience has shown that resins handling heavy concentrations of iron may become so contaminated that the exchange capacity for softening will be reduced far below the economic level.[36–38] There is some removal of iron, manganese, and aluminum from the resin during regeneration, but it appears to be a reaction at or near the surface only.

There are special applications where split-stream softening may be used to an advantage. The use is usually special and is not in wide general use. However, it does solve certain problems and does merit some attention. The process is of a dual nature in which a portion of the water is passed through a conventional salt regenerated exchanger, and the remaining water is passed through a resinous exchanger which has been regenerated with mineral acid. When regenerated with acid, the replaceable hydrogen ions are given up for calcium, magnesium, and sodium ions in the process. The net result is complete removal of these metals and destruction of the bicarbonates, thus leaving nothing but free carbon dioxide and water in their place:

$$Ca(HCO_3)_2 + H_2R \rightarrow CaR + 2H_2O + 2CO_2$$
$$Mg(HCO_3)_2 + H_2R \rightarrow MgR + 2H_2O + 2CO_2$$
$$2NaHCO_3 + H_2R \rightarrow Na_2R + 2H_2O + 2CO_2$$

When sulfates and chlorides are present, the corresponding mineral acids are formed by the exchange, thus:

$$CaSO_4 + H_2R \rightarrow CaR + H_2SO_4$$
$$MgSO_4 + H_2R \rightarrow MgR + H_2SO_4$$
$$2NaCl + H_2R \rightarrow Na_2R + 2HCl$$

The ratio of the two streams on remixing is adjusted so that the free mineral acidity formed in one is sufficient to neutralize and leave whatever degree of alkalinity is desired in the mixed effluent. Where special conditions of water composition and process needs are present, this method of softening may be desirable.

In addition to sodium and hydrogen cation-exchange softening, there is another application of exchange for softening known as "demineralization." This process employs both cation and anion exchangers in single or dual process tanks to completely remove all metal and nonmetal ions from solution. This method has not been applied to municipal water softening because of the economics involved. However, as exchangers and equipment improve, partial demineralization of municipal water supplies may become a reality for water quality improvement. As will be shown in a following chapter, demineralization is being used extensively in industry to produce water of extremely high quality.

Cation Exchangers

Not all of the ion-exchange materials discussed earlier are available for use today. Some have been replaced by newer materials, and others have been discarded because they no longer fill the need. The three exchangers which are used most today are greensand, siliceous gel-type zeolite, and the polystyrene resins. The first two enjoy only limited use and will not be discussed further. The reader is directed to several complete references dealing with these zeolites.[39–45] Since the polystyrene resins dominate the softening field, the discussion will be centered around them.

The polystyrene ion exchanger is a synthetic organic resin produced by a two-step manufacturing process. The basic mechanical particle is made by the polymerization of styrene and divinylbenzene (DVB) and takes the form of spheres. The spheres are then made ion-exchange-active by sulfonation. The product is washed, classified for particle size, regenerated with a sodium salt, and packaged for shipment ready to be installed in the water-softening equipment. A summary of the physical and operating characteristics of the polystyrene resins is given in Tables 10-2 and 10-3. The limits shown in these tables will include all brands of resin because they are produced under the same patent.[17]

The Softening-Regeneration Cycle

To accomplish the softening process, the ion exchanger must be confined in a vessel where the flow of water and regenerants coming to the unit can

TABLE 10-2 Physical Properties of Polystyrene Ion-exchange Resin

Appearance	White to reddish-brown
Form	Spheres
Cross linking, % DVB	8-12
Specific gravity	1.3 ±
Net weight as shipped, lb/cu ft	50-53
Moisture content as shipped, % by wt	35-50
Void volume, %	30-40
Effective size, mm	0.45-0.55
Uniformity coefficient	1.5-1.75

Sieve analysis (wet): U.S. Standard Sieve No. retained on	Range, % by volume	Typical, % by volume
16	2-5	3.7
20	20-35	36.3
30	35-55	42.1
40	12-22	14.3
50	0-4	3.1
—50	0-1	0.5

TABLE 10-3 Operating Characteristics of Polystyrene Ion-exchange Resin

Operating exchange capacity, kgr/cu ft	20-35
Recommended bed depth, in.	24-36
Softening flow rate, gpm/cu ft	2-6
Backwash flow rate, gpm/sq ft	5-6
Salt dosage, lb/cu ft	5-20
Brine concentration, %	8-16
Regeneration brine contact time, min	25-45
Rinse flow rate, gpm/cu ft	
Slow	1-2
Fast	3-5
Rinse requirement, gal/cu ft	20-40
Temperature, °F	up to 250

be controlled with a certain degree of accuracy. Softening equipment is designed to operate with either pressure or gravity flow. Pressure vessels for softeners are similar to pressure filters, and gravity softeners may be constructed of concrete, steel, or wooden stave tanks. Gravity softeners are usually confined to use where large capacity and areas are required. They are similar in design to the rapid-sand filters and lend themselves to ready inspection and maintenance. The pressure softeners operate downflow, while the gravity units may be operated either downflow or upflow. When operating downflow, the flow rate may be restricted by the head which is available. The head loss due to downflow resistance may be overcome by passing the water upward through the bed during the softening cycle. In either case proper freeboard must be provided to permit adequate head for downflow operation and room for expansion of the exchanger during upflow operation. Most of the softeners are of the pressure type in either horizontal or vertical steel shells. Large municipal water-softening plants use gravity softeners, softening upflow and brining downflow.

On completion of the softening cycle, the softener should be backwashed to loosen the ion-exchange resin, flush out any particulate matter which may have collected on top of the bed, and regrade the exchanger to make it more receptive to the regeneration cycle in preventing channeling of brine through the bed. Two to five min is sufficient for the backwash cycle. Manufacturers' engineering data give the time required and the recommended upflow rates to obtain maximum cleaning of the ion-exchange resin. However, final adjustments must be made on the individual installation to suit the conditions encountered. With gravity upflow softeners the backwash operation is eliminated.

In regenerating the pressure softener, brine is introduced to the bed at a controlled rate through a distributor system set immediately above the exchanger surface. To obtain maximum softening capacity from the ion exchanger, it is essential that the brine passes uniformly through and contacts all parts of the resin bed. Several different techniques are used in introducing brine to the softeners. In some small domestic softeners the tank is drained down several inches, and rock salt is dropped directly onto the top of the resin. Water is passed, at a controlled rate, through the salt to produce a brine of the proper concentration. In some cases the salt is allowed to stand for several hours to dissolve, after which water is introduced at the top to force the brine down through the bed. In better-quality domestic softeners and industrial units up to 1,000 cu ft, concentrated brine is pulled from the storage tank by water eductors and delivered to the brine distributor in the softener shell. The eductor water serves not only as the motive force but as a diluent to bring the brine to the proper concentration. The time of eduction determines the quantity of brine delivered to the unit.

In large gravity softeners the concentrated brine and dilution water are mixed and pumped to the brine distribution system over the bed. Both water and brine are metered and rate controlled to produce the desired concentration and quantity. In some installations water is left standing over the bed at the completion of the softening cycle. Concentrated brine is then pumped to the bed at a controlled rate while the spent brine is let out at a higher rate; thus, the water and brine mix and flow into the bed at the proper concentration. When this method is used, each process rate must be carefully controlled to produce the desired brine concentration and contact time to produce the optimum regeneration.

After the brine has been applied to the softener, all the spent brine must be removed before the unit is returned to service. This brine must be forced on through the ion exchanger to complete the contact time necessary for an efficient and economical regeneration. Rinse water is applied through the distributor piping or flooded over the bed from one end at the same rate of flow that the brine was applied. Because of the greater density of the brine it moves on down through the bed in a "piston" fashion. If rinsing were continued at this rate until the chlorides have dropped to an acceptable level where the unit can be returned to service, the time required would be excessive. After the optimum concentration of brine has passed from the unit, little is gained by prolonging the rinse time. The rinse rate is increased by approximately fivefold to complete the cycle. This quickly removes the last traces of chlorides and reduces the regeneration to half of what it would have been had the initial rinse rate been maintained (see Fig. 1). The quantity of rinse water needed to lower the chlorides to an acceptable level is dependent to a great extent upon the configu-

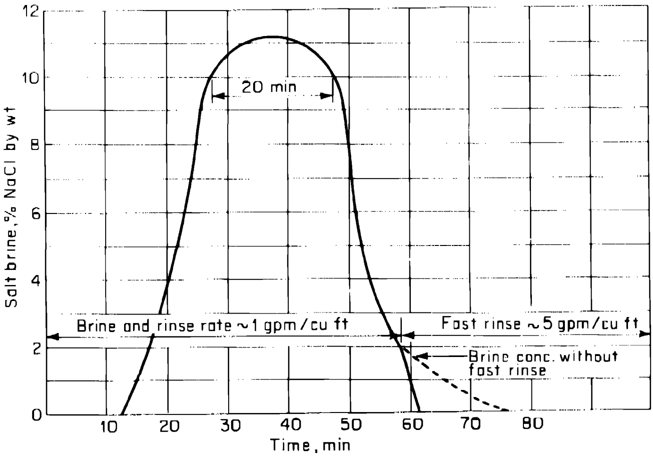

Fig. 1 Rinse flow rate as a factor in waste brine removal.

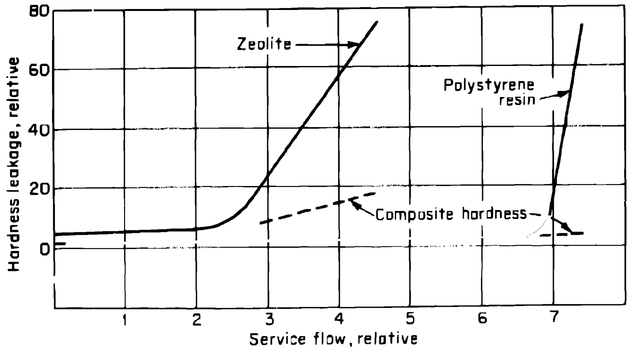

Fig. 2 Effect of softener overrun on water hardness.

ration of void space above and below the resin. It has been determined in practice that 20 to 40 gal of water per cubic foot of resin will be needed for rinsing. However, final adjustments must be made in the field to bring each installation to optimum operation. This adjustment is particularly important in treatment facilities where disposal may be a problem and where the cost of water may be a factor.

After completion of the regeneration cycle, the softener is returned to service by passing the hard water through the bed until a predetermined hardness breakthrough appears in the effluent. Although there have been a few attempts to operate pressure softeners upflow, the majority of them soften downflow. However, large gravity softeners may be operated upflow to reduce the head required to pass the water through them. When they are designed for upflow operation, it is customary to maintain a continuous and regulated flow so that the resin particles remain in full teeter throughout the run.

In those systems where the softened water is blended with unsoftened water to produce an intermediate hardness effluent, the softeners may be overrun. Since there appear to be no deleterious effects from almost complete exhaustion of the modern resins, additional economics can be gained from this practice. In Fig. 2 the softening cycle is carried past the point of normal hardness breakthrough. It will be noted that with the siliceous zeolites a greater percentage of water can be salvaged than with the polystyrene resins. This is due primarily to a difference in the rate of exchange in the two materials. If there are a large number of softeners in service, the effects of hardness due to overrun are hardly noticeable in the blended water. However, if there are only a few units in the system, this practice may enjoy only limited use and should be carefully studied before it is put into operation.

Performance Characteristics of Cation Exchangers

Compilation of the performance characteristics of all the ion exchangers could develop into a rather large volume of information. Although only the polystyrene resins will be discussed in detail, it should be noted that certain problem waters may be treated more effectively with the zeolites. An example would be where the size of an installation could not warrant both a filter and a softener for treating a hard, low-turbidity water. In this case a pressure softener filled with greensand or synthetic zeolite would provide both filtration and softening in one operation.

Operating data relating to the polystyrene resins have been developed from a number of sources. In each instance there has been an endeavor to test all factors which will affect resin performance. Operational data presented here are intended as a predesign guide to determine the general features of a proposed installation.

Rate of Flow in Gallons per Minute per Square Foot versus Gallons per Minute per Cubic Foot. As ion-exchange softening developed into an engineering process, it was so akin to filtration that the flows were naturally expressed as a function of the surface area. This serves the purpose, as it is related to the hydraulic characteristics of the particles during the backwash operation. Since the whole bed is involved in the ion exchange, a rate of flow in terms of unit volume becomes more significant. It should be noted that where hydraulics are concerned the flow rates will be expressed in gallons per unit area, and in all ion-exchange operations they will be expressed in gallons per exchanger volume.

Effect of Salt Dosage on Exchange Capacity. The most important factor in determining the exchange capacity of a softener is the amount of salt used in the regeneration. In engineering practice this is expressed as pounds of salt per cubic foot of exchanger. The capacity which can be expected from a polystyrene resin with various salt dosages is shown graphically in Fig. 3. A deviation of ±5 per cent from these data can be expected with a given salt dosage because the capacity is dependent upon such factors as per cent cross linkage of the resin, brine concentration time, and the concentration of sodium ions in the water.

Low dosages of salt result in the most efficient utilization of the regenerant. As the dosage is increased, the capacity can be increased up to the maximum limit of the exchanger. This wide difference in exchange capacity which can be obtained by the amount of salt used may be an important factor in design. In home and small industrial installations the cost of salt is insignificant compared to the advantage gained by a long softening cycle. Municipal and large industrial softening plants are more concerned with high efficiencies and low costs which can be gained from low salt dosages.

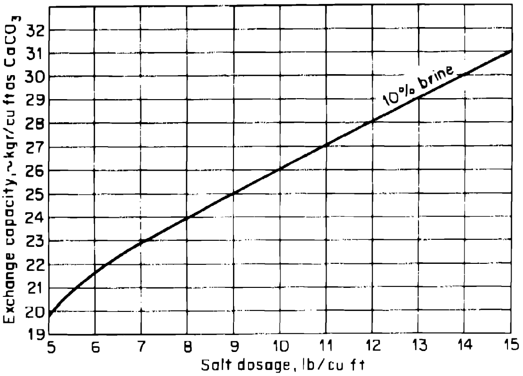

Fig. 3 Effect of salt dosage on exchange capacity.

To go much below 5 lb per cubic foot of resin may be inviting erratic operation. At low dosages the quantity of brine involved in the regeneration may become so small that to obtain the contact time essential, the flow rate drops to the point where there is not enough turbulence created in the bed to prevent streamlined channeling or short circuiting of the bed.

Effect of Brine Concentration on Exchange Capacity. There is an optimum concentration of brine which will produce the maximum exchange capacity in any resin. From manufacturers' data it would appear that this concentration should lie between 10 and 15 per cent (Fig. 4). As the concentration is increased, the resin particles tend to shrink, which inhibits the migration of the sodium ions through the particle matrix. As the concentration is decreased below the optimum level, there are fewer sodium ions available at any instant to displace the calcium and magnesium ions. If economy of operation is important, it is essential to determine this opti-

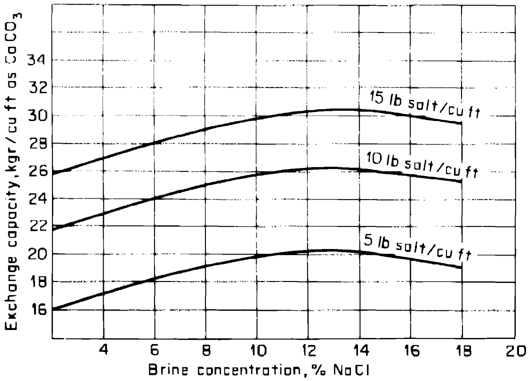

Fig. 4 Effect of brine concentration on exchange capacity.

mum concentration from either the manufacturer or from laboratory column tests at the installation. It should be noted that a concentration of 12 to 14 per cent will provide satisfactory regenerations.

In those installations which are close to the ocean, seawater regeneration may be economically feasible. This is equally true for those located near a supply of connate waters. Figure 5 shows the decrease in capacity which might be expected when using a dilute solution of pure salt brine. With connate or seawater the calcium and magnesium ions that are present interfere and cause a further decrease in the exchange capacity. There are installations in service which use connate water containing as low as 1.75 per cent salt, and a number are using seawater which may vary from 2.75 to 3.2 per cent sodium chloride. In Fig. 6 the exchange capacity is plotted as a function of the amount of seawater used.

Before seawater or connate water is used, it should be sterile and free of suspended matter. A polluted regenerant can cause fouling of the softener bed, followed by contamination of the softened water. In several Florida installations the seawater is filtered through rapid-sand filters and chlorinated before use.[46] Two plants in California draw seawater through a manifold placed below the ocean floor. The sand on the ocean bottom provides the filter media. Chlorine is applied at the pump discharge as the seawater flows to the clearwell. The use of the clearwell reduces the size of the pumping facilities and provides sufficient chlorine contact time for good sterilization. Where a constant supply of oilwell brine is available, a study to determine the feasibility of using this brine for regeneration should be made. Equipment would be needed to completely remove all oil and odor from the brine. This could be a cooperative effort with the oil company to share costs in the salvage of the brine as a regenerant and disposal of the spent brine.

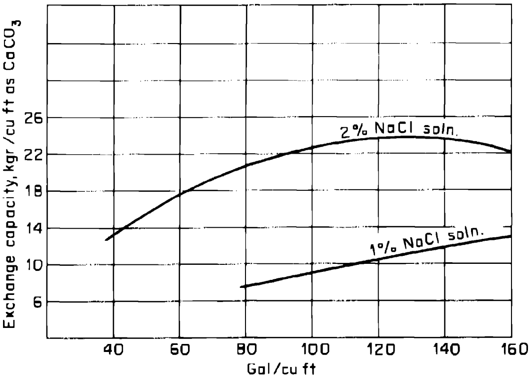

Fig. 5 Effect of dilute brines on exchange capacity.

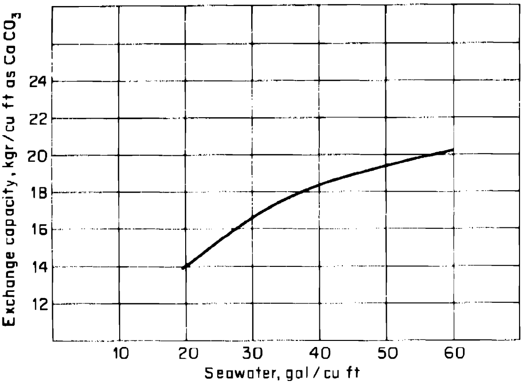

Fig. 6 Exchange capacity with seawater regeneration.

Brine Reclamation. Economics can be gained in the operation of certain installations by reusing a portion of the partially spent brine in the following regeneration. In general the first one-third of the spent brine that comes from the softener contains approximately 80 per cent of the hardness. The second one-third of the brine is high in sodium and contains the remainder of the hardness that is being removed. The last portion contains the last traces of salt washed from the bed. The salt content of the middle portion is high enough that it can be used in a subsequent regeneration. It may be used to backwash the exchanger, or it may be used initially in a regeneration followed by sufficient fresh brine to attain the desired capacity. Reduced salt costs and a reduction in the amount of spent brine requiring disposal are factors to be considered in favor of brine reclamation. Against these must be weighed the cost of additional piping and pump equipment and space requirements for the spent brine holding tanks.

Effect of Brine Contact Time on Exchange Capacity. The brine contact time may be defined as the interval between the time the brine passes a point in the bed and that arbitrary moment at which the rinse water passes the same point. There are many definitions of contact time, but like this one they are all relative and serve the same purpose. As shown by the data in Fig. 7, the best results are obtained when the contact time is 20 to 35 min. For a 10 to 15 per cent brine this would represent a flow rate less than 1 gpm per cubic foot of exchanger. Flows in excess of this tend to reduce capacity; in like manner, but not to the same extent, rates less than 0.15 gpm per cubic foot, again result in a reduction of exchange capacity.

Effect of Bed Depth on Exchange Capacity. Bed depth does not appreciably affect the exchange capacity of a resin because the reaction rate during softening is so rapid. Figure 8 shows the increase in capacity which

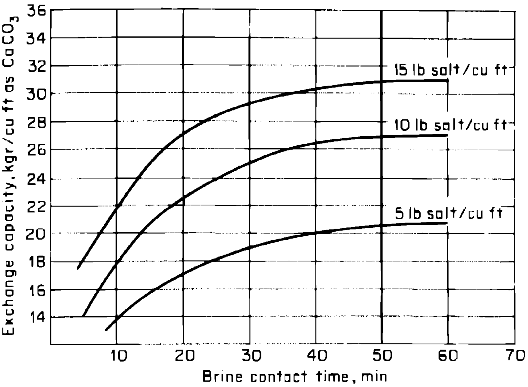

Fig. 7 Effect of brine contact time on exchange capacity.

can be expected as the depth of the bed is increased when softening downflow. These data were produced with a hard water feed rate of 2.5 gpm per cubic foot (4 to 10 gpm per sq ft), which appears to be about the average rate used in softener operation. Lower rates flatten the curve slightly, and at higher rates the curve retains the same shape but shows a lower capacity. In upflow operation the effect of bed depth is even less noticeable. The bed will expand up to 35 to 50 per cent when it is operated upflow, and because of the more intimate contact of each particle with the water, the effect is the same as if the bed depth were increased.

Effect of Water Composition on Softener Performance. The composition of the influent water may have a marked effect upon the capacity and hardness leakage of the resin. As noted in the chemistry of softening, the calcium and magnesium ions exchange for sodium ions on the resin. In

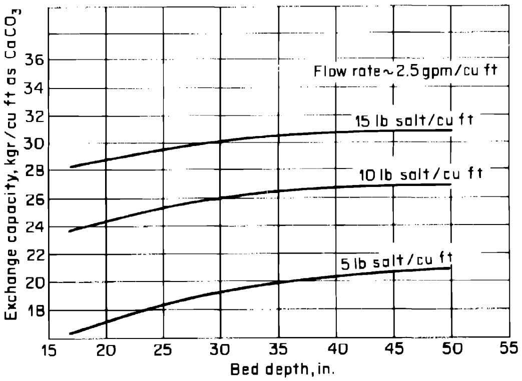

Fig. 8 Effect of bed depth on exchange capacity.

regeneration the reverse reaction takes place. It can be assumed that at some theoretical sodium-hardness ratio neither softening nor regeneration can take place. Hardness alone in the influent water has little effect upon the capacity of the resin. As the sodium content increases, competition develops between the sodium and hardness ions for the active sites on the resin. In most water supplies the sodium-hardness ratio is low, and the effect upon capacity is hardly noticeable. In Fig. 9 the effects of increasing hardness in a water with a sodium-hardness ratio of 1:3 are plotted as a function of capacity. Only when the sodium-hardness ratio exceeds 2:1 will there be any real need to be concerned about the lowering of capacity due to decrease in influent water quality. As this latter limit is approached, there should be more concern about the quality of the finished water than in the process.

As an increase in the sodium-hardness ratio causes a decrease in exchange capacity, it also causes an increase in the hardness leakage of the softener. In those installations where the final water needs to be extremely soft this may be a problem, as indicated in Fig. 10. In municipal plants, where the softener effluent is mixed with unsoftened water to produce an intermediate hardness, leakage is no problem. Softening of problem waters alone without additional treatment should be thoroughly investigated before the final design is made.

Effect of Service Flow Rate on Capacity. Since exchange occurs so rapidly in resins, the operating capacities are little affected by increasing service flow rates up to as high as 10 gpm per cubic foot (Fig. 11). There are reported installations which are operating in excess of 15 gpm per cubic foot. To maintain good hydraulic flow through the softener bed, it is better to hold a steady flow rate in the 2 to 4 gpm per cubic foot range than to design for higher intermittent flow rates. In many waters there is enough

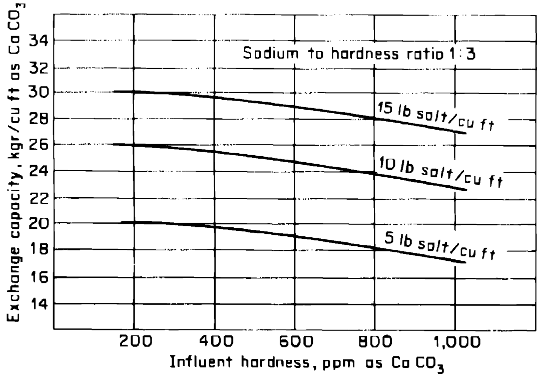

Fig. 9 Effect of water composition on exchange capacity.

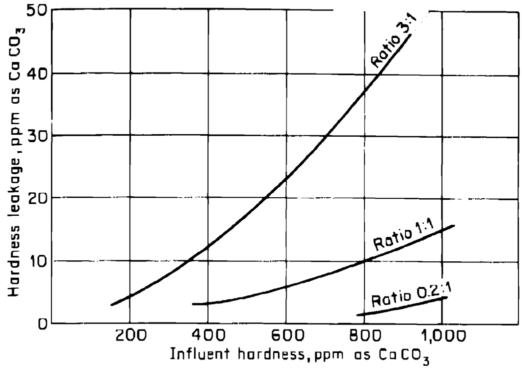

Fig. 10 Influence of water hardness and sodium to hardness ratio on hardness leakage.

turbidity in the water to cause excessive head loss and channeling due to buildup of this material on the surface of the unit. In upflow operation excessive rates of flow are not to be encouraged because of the danger of loss of resin due to carryover. In intermittent industrial or domestic softeners the flow rates may rise to the maximum hydraulic capacity of the unit for short periods, provided this is followed by a period of inactivity in which the resin can "recover." High rates should never be attempted with zeolite or greensand. Another factor involved in high-rate softening is the pressure drop developed across the bed. Figure 12 shows the pressure drop across a resin bed as a function of both service flow rate and temperature. Other factors such as the size, shape, and size distribution of the resin particle will have a pronounced effect upon the pressure drop. As long as the in-

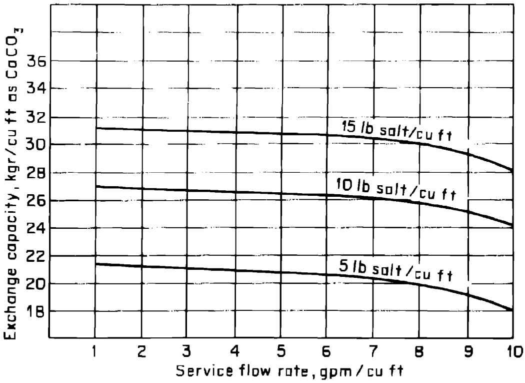

Fig. 11 Effect of service flow rate on exchange capacity.

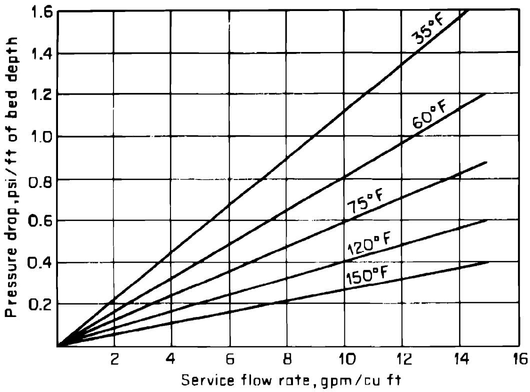

Fig. 12 Effect of downflow service rate on pressure drop.

fluent water is low in turbidity and the bed remains relatively clean, pressure drop should be of little concern.

Effect of Temperature on Performance. A change in water temperature will have an effect upon the pressure drop (as indicated above), will affect the degree of expansion during backwash, and will affect the exchange capacity. In operation the variation in exchange capacity has been as much as 2.5 kilograins per cubic foot from summer's peak temperature to the lows of winter. This is shown in Fig. 13, where the exchange capacity in one softener unit is plotted for a 3-yr period. In most cases this 10 per cent deviation will not significantly affect operation.

Backwash Flow Rate. To maintain the hydraulic characteristics of an ion-exchange resin in good condition, the softener should be backwashed after each softening cycle. Foreign matter can be removed from the resin

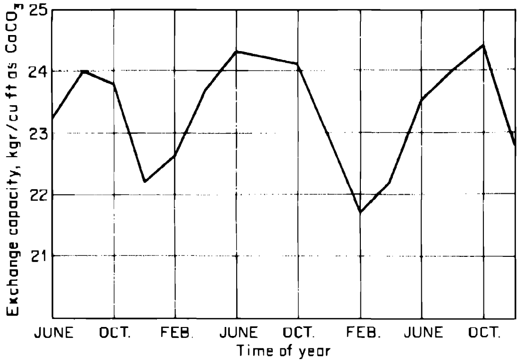

Fig. 13 Effect of seasonal temperature changes on exchange capacity.

most effectively when the backwash rates are sufficient to give 50 to 75 per cent expansion of the resin. The rate requirement will be affected by the relative densities of the resin and water. These will vary with water temperature. Figure 14 relates bed expansion to flow rates for a typical commercial resin at temperatures from 35 to 170 °F. It may be necessary to make an occasional adjustment in the backwash rate to correct for seasonal temperature changes to prevent the loss of resin or to maintain sufficient flow to keep the bed clean. The equipment should be designed to provide adequate freeboard for at least 75 per cent expansion without the resin being washed to waste.

It has already been indicated that the softener influent should be free of turbidity and suspended matter. There are conditions under which a certain amount of turbidity will reach the bed. The nature of the turbidity and the manner in which it is laid down on and in the resin will determine the rates which should be used in backwashing. The more tenaciously it is held to the resin, the greater the backwash rates should be. However, this is not always true. Dual backwashing rates may be employed in which the initial rate is held low to allow the resin particles to work just enough to rub and scour against each other. After the foreign matter has been rubbed loose, the rate is increased to fully open the bed and allow this material to be carried out.

Limitations

Iron, Manganese, and Aluminum. Iron in the softener feedwater, in either the precipitated or solution form, will seriously affect the exchange capacity of the resin. The problem is compounded by the fact that iron in water can take so many forms. Iron in the ferrous state will be removed

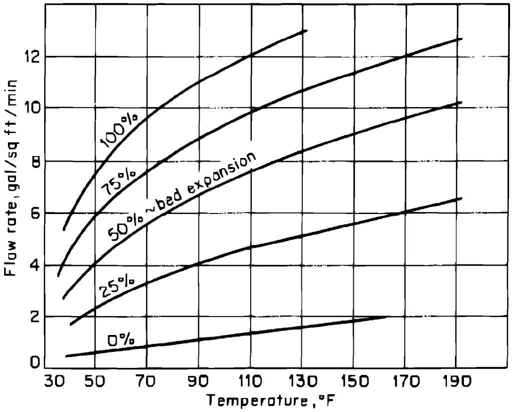

Fig. 14 Bed expansion as a function of backflow rates and temperature.

from solution by ion exchange. If the iron remains in this form on the resin, it may be removed and flushed to waste with the subsequent regeneration. This appears to take place almost entirely at the surface of the particles. Some of the iron ions are exchanged deep within the structure of the resin particle. Here the iron may be oxidized by dissolved oxygen to a stable nonexchangeable form. Hardness, chlorine, and pH of the water can intensify the problem. After this occurs, no amount of salt brine will remove the internally precipitated iron oxide. In iron-bearing waters this one-way exchange may continue until most of the operating exchange capacity is lost.

If the iron is oxidized prior to softening, and the resulting gelatinous ferric hydroxide is not removed, it will be filtered out on or in the resin bed. Removal of the flocculent precipitate from the softener bed will present problems. If sufficient time elapses after the iron is precipitated until it contacts the softener, it will change from the hydroxide to an oxide form. The gelatinous property will be lost, and the iron will be filtered out by the bed. Most of this debris iron will be removed during backwashing.

The iron which precipitates on the inside of the resin beads or which sticks to the outside causes them to take on a dark red (rusty) appearance. If iron is present in the softener influent, a serious loss in exchange capacity may be lessened by contacting the resin with a solution of sodium bisulfite ($NaHSO_3$) or sodium hydrosulfite ($Na_2S_2O_4$). These chemicals may be mixed with the regeneration brine and the cleansing operation accomplished along with the regeneration. However, it would be well to consult the resin supplier before undertaking this chemical rejuvenation method.

Severe cases of iron fouling can be effectively handled by treating the resin with dilute hydrochloric or sulfuric acid. This method is not generally recommended unless the equipment and piping are made of corrosion-resisting materials.

Manganese in natural waters and aluminum resulting from incomplete precipitation of alum during pretreatment will cause resin fouling and loss in exchange capacity. Since these two are normally present in lower concentrations, they are not as troublesome as iron.

Iron and other chemical fouling can be minimized in the operation of municipal and industrial softeners by pretreating the water. Methods which may be used include: (1) aeration and filtration, (2) chemical coagulation or oxidation and filtration, (3) chlorination and filtration, or (4) use of manganese greensand filters without pretreatment. These methods of treatment are described in other sections of this book.

Turbidity and Bacterial Slimes. Poor operation and loss of exchange capacity in the cation exchanger can be caused by organic or inorganic turbidity in the water, which coats the resin particles. It has been shown that bacterial slimes will coat resin particles when proper sterilization has not been practiced.[22,23] The problem resulting from turbidity and bacterial slimes may be a loss in exchange capacity due to the coating which mechanically blocks the surface of the particles, or it may result in excessive head loss due to deposition of foreign matter at or near the surface of the softener.

Debris which is large enough to be retained on the surface of the bed may be removed by backwashing. However, debris which will carry down through the bed can coat the resin particles and require special methods for removal. Care should be exercised where turbidity is encountered to either remove the material before passing the water to the softeners or to provide special cleaning operations along with the regeneration.

Should bacterial slimes develop within a softener, they can be eliminated by chlorination of the feedwater or by the application of liquid bleach along with the regenerant each time the unit is regenerated. Coatings of bacterial slimes may be removed by applying warm caustic solution to the resin. The softener is allowed to stand for several hours and is then backwashed to remove the dead slime from the bed.

Oxidizing Agents. Chlorine is the only oxidizing agent normally encountered in potable waters. The use of tests and operating data have shown that normal dosages of chlorine will have minimum effect upon the resin.

Structural breakdown of the basic bead has been found in some of the polystyrene resins after extended high-rate operation. The first noticeable sign is a gradual increase in resin volume. At first there is a slight decrease in exchange capacity as the volume increases. In time a total reduction in the overall capacity becomes pronounced.[47]

Swelling of the resin results from breaking of the cross-linking bonds in the basic resin matrix. The chlorine appears to be the big contributor to bond failure. The water-holding capacity of the resin increases as more and more of these bonds are broken. Attrition results as the soft surface of the swollen particle is swept away.

The basic structure of the matrix probably has a great deal to do with the stability of the resin. As the per cent cross linking is increased, the resin displays more resistance to oxidation. However, when the cross linking is carried much above 12 per cent, the resin particle becomes so dense and "tight" that there is a serious loss in exchange capacity. In Fig. 15 two typical commercial resins are shown in which the exchange capacity and volume are plotted against the cumulated flow. Case *A* shows rather severe de-cross linking resulting in a measured volume increase and exchange capacity loss, while in Case *B* there appears to be little effect in the same time. Both resins were placed in operation at the same time and have continued to operate for 14 yr under identical conditions. In domestic operation this should not be a problem. For municipal operation the pres-

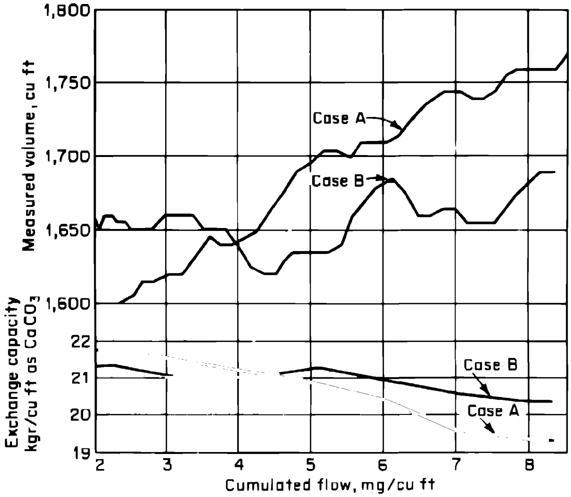

Fig. 15 Effect of de-cross linking on resin volume.

ent-day polystyrene cation resins should have an economic life in excess of 15 to 20 yr.

High chlorine residuals resulting from iron removal by oxidation can cause rather severe loss of resin. If this type of treatment is used for iron removal, the chlorine should be removed prior to softening.

Temperature. Polystyrene resins may be operated at up to and including 100 °C. If the resins are operated at 100 °C for an extended period, care should be taken to remove the dissolved oxygen and chlorine to prevent breakdown of the resin. Softening at temperatures greater than this is possible, but before it is attempted the resin manufacturer should be consulted.

pH. There appears to be no limit on the pH of waters to be softened or on the regenerants, since the polystyrene resins will operate equally well in high and low pH water. There are serious limitations on pH where the zeolites are concerned.

DESIGN OF SOFTENING EQUIPMENT

Design of a softening system must be based upon the flow, influent water quality, effluent water quality requirements, resin exchange capacity, resin hydraulic characteristics, period of time between regenerations, type of operation (manual or automatic), and number of units to be installed.

Equipment Size. In the sizing of softener units it is essential to first determine the volume of ion exchanger required. Babbitt[48] formulates this as:

$$E = \frac{KQH}{G}$$

where E = volume of exchange material to be used, cu ft
Q = volume of water to be treated between regenerations, cu ft
H = hardness of water, grains per gal
G = hardness to be removed between regenerations per unit of volume of exchange material, grains per cu ft
K = a factor dependent on the units; 7.48 for units stated in formula

In manual operation consideration should be given to calculating Q to make the regenerations fall during the day when labor can be used most effectively. Shell diameter and bed depth should be adjusted to maintain a unit rate in the range of 4 to 8 gpm per square foot. Automatic softeners will present certain savings in reduced equipment size and labor cost. These savings will be offset by an increase in equipment cost. The specific installation will require study to determine the best method of service to use in light of the intended service. Normally pressure-type softeners are used in industrial or small municipal installations where high flow rates and small space requirements are essential. Large municipal installations find economy and ease of operation and inspection in gravity softeners. In either case the same principles of cyclic operation apply.

Construction Details

Since the majority of all cation-exchanger softeners are of the downflow pressure type, only their construction details will be described.

Shells. Pressure softeners may be either the vertical or horizontal type, usually employing a steel vessel. The vertical units vary in diameter from 8 in. to 10 ft. The upper diameter is limited by shipping restrictions. Horizontal softeners are made up to 10 ft in diameter and 25 to 30 ft long. Hydraulic distribution, restricting head room, and loss in exchange capacity due to the inability to fully utilize the resin in the bulges at the side and ends of the vessel limit the use of horizontal softeners. In either vertical or horizontal design the shell consists of a steel cylinder with dished heads and a manhole or handhole for access to the inside of the vessel. The interior of the vessel should be coated with a chemically resistant lining to afford maximum metal protection against the corrosive environment of the regenerates. Some of the smaller units are galvanized; however, recently most of the units have been plastic lined. All internal and external piping should be selected for their ability to resist corrosion. A recent survey has indicated that 95 per cent of all piping on salt regenerated softeners is either plastic or red brass.

Underdrain System. In the bottom of the softener is a drain system which collects the water during softening, distributes the water for backwashing, and collects the brine and rinse water during regeneration. One of the most important features of the underdrain system is that it must be designed to evenly collect or distribute the flows during any one of the multiple operations. During softening an even collection will ensure full utilization of the resin capacity. Uniform backwash distribution will bring all parts of the bed into operation and prevent channeling. On the brining and rinsing operation, an even drawoff is essential so that complete regeneration can be assured and none of the brine will be left in the softener to deteriorate the softened water quality. The design of underdrain systems assumes many variations to accommodate the size and shape of the vessel. The systems usually take either the deflector-plate type or the lateral-manifold type. In the former, a specially designed deflector plate is installed in the bottom so the perforated edge is mounted a specific distance from the vessel bottom. Stiffeners are added to support the weight of the gravel and resin. The discharge from the vessel is taken from underneath the deflector plate. This design takes advantage of the volume of the dished bottom in which to install the plate. The manifold-lateral system is made up of a manifold pipe connected to the outlet with smaller laterals connecting to the manifold and so spaced to effectively cover the cross section of the vessel. Openings into the manifold-lateral piping may be strainers or drilled holes. A subfill of concrete is placed in the bottom to prevent pocketing of the brines and provide support for the laterals and strainers. Several manufacturers build softeners in which the deflector plate is perforated with many small openings, which eliminates the need for a bed of gravel over the underdrain to support the resin.

Gravel. The gravel which is placed over and around the underdrain is as important in the even distribution of the flows as it is in supporting the ion-exchange material. It tends to further break up the flow into smaller components to give an even flow over the entire cross section of the vessel. The gravel is usually placed in several layers, with the coarse material on the bottom and the finest at the top. The type of underdrain system will affect the size of gravel to be used. Deflector plates require 1-to-1 ½-in. gravel over and around the plate, a 4-in. layer of ½-to-1-in. gravel, and a 4-to-5-in. layer of ¼-to⅛-in. gravel. For manifold-lateral systems, a layer of ¼-to-½-in. gravel is placed around and is allowed to extend 5 in. above the header, and then a 5-to-6-in. layer of ¼-to-⅛-in. gravel completes the gravel support.

Ion-exchange Bed. An ion-exchange bed, varying in depth from 20 to 60 in., is placed on the supporting gravel. It is hydraulically leveled and classified by the initial backwash. The largest particles will be resting on the gravel, and the finest will be at the top of the bed. Immediately above the bed and below the washwater collector a freeboard space must be provided to allow the resin to expand without being carried out of the vessel. This expansion height should be 80 to 100 per cent of the bed depth to provide adequate volume for expansion of the resin under all backwash conditions.

Service Water Inlet and Washwater Collector. The service water inlet and washwater collector is placed in the upper part of the vessel. This single inlet-outlet serves to introduce the water for softening and rinsing and to collect the wastewater during backwashing. It is baffled so the incoming water is caused to flow out evenly over the softener surface, thus preventing the incoming water from disrupting the surface of the softener bed.

Brine Inlet System. The brine distribution manifold is placed immediately above the softener bed. At this location it serves to uniformly introduce the brine directly to the surface of the softener so that the brine will contact all parts of the bed. In most domestic and industrial softeners saturated brine is picked up from the salt-dissolving tank, diluted to the proper strength, and introduced into the softener by hydraulic ejectors. In large installations pumps may be used to introduce the brine. Where the brine is pumped, provisions must be made to dilute the brine before it enters the softeners. On entering the softener, it is further diluted by the water which is left standing over the bed. Care should be taken to make sure that the brine passing through the bed is of the desired strength. This can best be assured by determining the concentration of the spent brine as it leaves the softener.

Operational Controls

Backwash. Backwashing should be carefully controlled to maintain the correct rate of flow to properly clean and loosen the bed and prevent loss of the resin by carryover. The rates may be controlled by means of (1) a rate of flow controller in the backwash inlet line or (2) a control valve in the backwash discharge line. In domestic units the rate is controlled by an adjustable or fixed orifice in the backwash inlet line. After the rate is once set, it is assumed that the supply water pressure will remain constant. Wash rates in domestic units are not as critical as for the industrial and municipal units.

Rinse. The control valve which was used for controlling the backwash rate of flow may also be used to control the slow- and fast-rinse rates.

Meters. A meter is usually included in the effluent line as standard equipment on all large industrial and municipal softeners. In automatic service the meter is equipped with an electrical contact which starts the regeneration cycle after the passage of a preset volume of water. During regeneration the electrical component of the meter resets automatically for the next softening cycle. On manual softeners an electrical contact is made in the meter which gives an alarm at the end of the softening cycle. These meters are reset manually as a part of the manual regeneration operation. Meters may also be used during the regeneration to measure the amount of brine and dilution water necessary. Small domestic units meter regeneration solutions through orifices on a time basis.

Gravity Softeners. In municipal water softeners of the gravity type, the volume of resin may vary from a minimum of 500 to a maximum of 4,000 cu ft per softener. In general the design is identical except the vessel is made of concrete rather than steel, and the water may pass upflow during softening and downflow during regeneration. Upflow softening is used to reduce the head requirements necessary to force the water through the softener bed, and it eliminates the need for backwashing the softener before regeneration. Since economy of operation is extremely important in large municipal installations, all service and regeneration flows are metered and frequently corrected to maintain the most economical operation. Care must be exercised in the design of inlets and outlets of these softeners to ensure that all solutions are uniformly distributed to or withdrawn from the softener.

Brine and Wet-salt Storage Tanks. Tanks or basins for the dissolving of salt and storage of brine can take several different forms, depending to a great degree on the size of the softener to be served. In domestic and small industrial softeners, the brine tank serves both as a salt storage and concentrated-brine storage tank. During the brining cycle the concentrated brine is withdrawn from the bottom of the tank while freshwater is introduced at the top. An excess of undissolved salt in the tank ensures an ample supply of concentrated brine. In large installations the salt is dissolved in a wet-storage basin or tank, and the brine is transferred to a holding tank from which it is introduced into the softener. The wet-storage basin is desirable in an installation requiring large quantities of brine. The capacity of these basins varies from several tons up to many carloads of salt. Salt handling can be reduced to a minimum if the storage tank is designed to drop the salt directly into it from the rail car or truck.

In large municipal installations additional economy can result if unrefined rock salt is used. This salt will carry with it a small amount of sand and silt which must be removed before it can be used successfully in the softeners. The sand can be removed with a minimum of effort. However, silt removal does present more of a problem. Where rock salt is used, wet storage is essential. If the brine is drawn from the wet storage in a completely saturated condition, on standing, 95 per cent of the suspended silt will settle out within 30 min. The clarified brine is then filtered and stored ready for use. If large tonnages of salt are to be dissolved, consideration should be given to flowing the dissolving water up through the salt. The concentrated brine, which carries the silt, is allowed to flow into a holding tank where the silt settles. Clarified brine is drawn from the top of the tank for filtration. The sand separates from the brine and remains in the dissolving basin. Occasionally it is necessary to remove both the dissolving and sedimentation tanks from service for cleaning. This method has been used by one large municipal plant to dissolve as much as 103,700 tons of rock salt yearly.[49]

Disposal of Spent Brine

One of the greatest problems created by ion-exchange softening is the disposal of the spent brine from the regeneration cycle. These waste products are composed principally of the chlorides of calcium, magnesium, and sodium. Small quantities of iron, manganese, and aluminum may be present. The uncontrolled discharge of these wastes into waterways can cause damage to fish life. Although certain fish may be able to tolerate high concentrations of salts for a short period, good aquatic life can be maintained only when these concentrations are held far below the short exposure, high-toxic-concentration level. In addition to the damage to aquatic life the brines degrade the quality of the stream and make it less desirable for downstream users of the water. Discharge of regeneration brines into ponds can cause irreparable damage to the groundwater supply into which the brines may infiltrate.

Waste brines flowing into a sanitary sewer system may seriously upset the biological process. This is especially true should a "slug" of highly concentrated brine flow directly into the sewage-treatment plant. Corrosion of mains, pumps, and equipment is also a factor when brines flow into the sewer system.

The total wastewater may vary from 1.5 to 7 per cent of the amount of water softened. The wastewater will contain chlorides in direct ratio to the amount of salt used. The amount of salt to be disposed of in the wastewater may be approximated by the formula $C = 35SH$, in which C represents the chloride ion, expressed in pounds per million gallons; S is the salts, in pounds per thousand grains of hardness removed; and H is the reduction of hardness, in parts per million as calcium carbonate.[50] The total dissolved solids in a composite sample of a typical spent brine may vary from 35,000 to 45,000 ppm, while the maximum instantaneous concentration of ions in the discharge may vary from 95,000 to 120,000 ppm.

In the face of the growing interest in the prevention of freshwater pollution every effort should be made to provide for adequate and safe wastewater disposal where cation-exchange softening is being considered. The problem should be discussed and cleared with the applicable regulatory agency.[51,52]

Several disposal methods have been proposed and discussed. Haney[52] suggests the possibility of using evaporation ponds, uncontrolled dilution, controlled dilution, and brine disposal wells. Another method is discharge to tidewater when plant location makes this feasible.

Evaporation Ponds. Net yearly solar evaporation rates, in excess of rainfall, may vary from a maximum of 60 to 70 in. per year in the semiarid southwest to a negative amount in the rainy belts. Evaporation ponds should be watertight to prevent the flow of brine into freshwater aquifiers. This method is questionable because of the nonuniform year-around evaporation rate, large land area requirement, and the expensive construction required to make the basin watertight.

Uncontrolled Dilution. Discharge of the waste brine into a waterway offers the most economical means of disposal, provided certain conditions are available. The amount of natural water flowing in the stream must be great enough to dilute the salt brine to a level which will not endanger the aquatic life or deteriorate the water quality where it must be used beneficially downstream. Before this method is sanctioned by the governing regulatory agency, evidence will have to be provided to show that there is sufficient water for dilution during minimum stream flow.

Controlled Dilution. Disposal by controlled dilution requires storage of the waste brine and controlled discharge into the stream to keep the ion content of the stream no higher than the maximum allowable level that has been set. The same requirement is true for discharge into a sewer system. If the flow in the stream is variable, long-term storage may have to be considered.

Brine-disposal Wells. Brine wells may provide a means of disposing of limited quantities of spent brine. This technique has not been used to any extent in the water-treatment field. However, oil companies have satisfactorily used this method to dispose of brine resulting from oil production. Before waste can be injected into the ground, it must be treated to prevent suspended matter from plugging the pores of the formation which is to receive it. It should be conditioned to prevent corrosion of the well casing and also to prevent it from reacting with the receiving formation to form a precipitate.

The geology of the region will determine the depth of disposal wells. The point of injection should be such that there is no danger of contamination of existing potable wells. This requires special construction of the well to prevent the waste brine from following the outside of the casing toward the surface. These wells may be as shallow as 400 ft or as deep as 10,000 to 15,000 ft. The latter case would be out of the economic range for a softening plant. However, if an ion-exchange softening plant is being considered where there is a large number of producing oil wells, an agreement may be made with the oil company to dispose of the spent brine where they are required to return water to the voids left by the oil. By mutually sharing in the disposal and recharge problems, an economic advantage may be available for the softening plant and the oil producer.

The type of treatment required for the brine will influence the cost.

Treatment may involve any number of the standard water-treatment processes such as aeration, coagulation, sedimentation, and filtration. Treatment for removal of iron and manganese will be essential if these elements are contained in any appreciable quantity in the water being softened.

Ocean Disposal. The ocean may offer the best method of disposal for those plants which are geographically so located. Plants in Florida, New Jersey, and California are using this method. For those plants right on the ocean this is the obvious means of disposal; but as the plant location moves further inland, disposal costs rise. In 1941 the Metropolitan Water District of Southern California put into operation an ion-exchange softening plant some 50 miles from the ocean. There were no rivers available for discharge. It was necessary to build a disposal line 22 miles long to intercept one of the county ocean disposal sewers. The district pays a fee for the right to discharge into the sewer. Had the sewer not been available, it would have been necessary to extend the line on to the ocean. The amount of waste brine has increased in volume from 300,000 gpd in the first stage of construction to slightly over 7 million gpd at the maximum design capacity of the plant.

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11

Iron and Manganese

By JOHN T. O'CONNOR

EFFECT OF IRON AND MANGANESE ON WATER USE

The presence of iron and manganese in water is objectionable primarily because the precipitation of these metals alters the appearance of the water, turning it a turbid yellow-brown to black. In addition, the deposition of these precipitates will cause staining of plumbing fixtures and laundry.

Another condition which has been associated with the presence of iron and manganese in water supplies is the growth of microorganisms in distribution systems. Accumulations of microbial growths can lead to reductions in pipeline carrying capacity and the clogging of meters and valves. Sloughing of the accumulations often leads to adverse consumer reaction including complaints of tastes and odors. Depositions of iron and manganese precipitates in mains are frequently resuspended by increased flow rates causing high turbidities.

Iron and manganese themselves in concentrations greater than several milligrams per liter will impart a taste to water which is described as metallic, astringent, or medicinal. Finally, the precipitation of these metals may lead to difficulty with water-treatment processes such as ion exchange. This can be particularly aggravating to the owner of an individual household-treatment unit.

Because of the nuisance caused by relatively small concentrations of these metals, many groundwater supplies for municipalities, industries, and individual homes require treatment for the removal or control of iron and manganese. Where ion-exchange softening is practiced, iron and manganese are frequently removed prior to exchange because the precipitates formed would cause clogging problems and would coat the exchange medium, resulting in an accelerated loss in exchange capacity.

Comparatively few surface waters require treatment for the removal of iron and manganese from solution. Those surface supplies which do require such treatment are generally derived from the hypolimnion of deep lakes or from eutrophic lakes where reducing conditions have developed to the extent that deposits of precipitated iron and manganese are returned to solution. Frequently this is a seasonal or short-term problem. In some instances, the discharge of acid industrial wastes or mine drainage will create conditions whereby iron is found in solution in waters containing oxygen. For the most part, however, it is the groundwater supply which receives treatment for iron and manganese removal.

Occurrence of Iron and Manganese in Natural Waters

The presence of iron and manganese in groundwaters is generally attributed to the solution of rocks and minerals, chiefly oxides, sulfides, carbonates, and silicates containing these metals.

Iron occurs in the silicate minerals of igneous rocks. Pyroxenes, amphiboles, and some micas generally contain iron. It also occurs in the form of various oxides, such as magnetite (Fe_3O_4), hematite (Fe_2O_3), and limonite ($2Fe_2O_3 \cdot 3\,H_2O$). The sulfide and carbonate minerals are also important sources of iron. These include pyrite (FeS_2) and siderite ($FeCO_3$).

Manganese is found in greatest abundance in metamorphic and sedimentary rocks. Only small amounts are found in igneous rocks. Manganese oxides such as manganite (MnOOH), pyrolusite (MnO_2), and hausmannite (Mn_3O_4) will accumulate in soils as the more soluble constituents are leached from weathered rocks. Rhodochrosite ($MnCO_3$) is particularly important in manganese equilibria in natural waters. Alabandite (MnS), on the other hand, appears to be of lesser importance. Table 11-1 lists some of the important iron- and manganese-bearing minerals.

The fact that manganese-bearing minerals are less abundant than iron-bearing minerals in part accounts for the fact that iron is found more frequently than manganese in groundwaters. The hydroxides and carbonates of Mn(II) are, however, somewhat more soluble than those of Fe(II). Despite this, the concentrations of iron and manganese found in groundwaters do not often exceed 10 mg/l and 2 mg/l, respectively.

Although not typical of all regions in the United States, some idea of the concentrations of iron and manganese encountered in groundwaters can be

TABLE 11-1 Iron- and Manganese-bearing Minerals

Formula	Mineralogical name
$Fe_{0.95}O$	Wüstite
Fe_2O_3	Hematite
$2Fe_2O_3 \cdot 3H_2O$	Limonite
Fe_3O_4	Magnetite
FeS	Troilite
FeS_2	Pyrite
$FeCO_3$	Siderite
Fe_2SiO_4	Fayalite
$FeOOH$	Goethite
MnO	Manganosite
Mn_3O_4	Hausmannite
γ—$MnOOH$	Manganite
β—MnO_2	Pyrolusite
$MnCO_3$	Rhodochrosite
MnS	Alabandite
$MnSiO_3$	Rhodonite
Mn_2SiO_4	Tephroite

obtained from Fig. 1, which shows the distribution of iron and manganese in groundwaters used for municipal water supplies in Illinois.[1] In this instance the concentrations of iron encountered are roughly 10 times the concentrations of manganese.

Mechanism of Solution

The solution of iron- and manganese-bearing minerals is often attributed to the action of carbon dioxide in groundwaters. Most of the carbon dioxide is presumably generated by the bacterial decomposition of organic matter

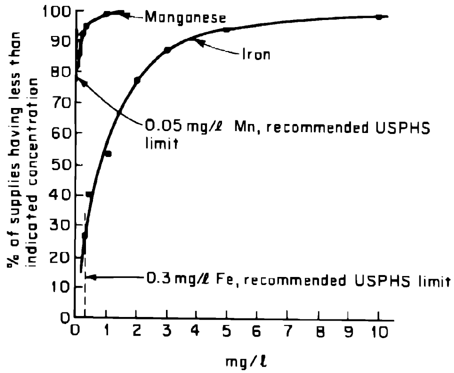


Fig. 1 The distribution of iron and manganese in 770 municipal groundwater supplies in Illinois. (*Data from Illinois State Water Survey, Circular 90, 1963.*[1])

leached from the soil. The solution of these minerals may take place under anaerobic conditions and in the presence of reducing agents (organic substances, hydrogen sulfide) capable of reducing the higher oxides of iron and manganese to the ferrous, Fe(II), and manganous, Mn(II), states.

Similar conditions are believed to be responsible for the solution of iron and manganese from the sediments of stratified lakes.

Figure 2 is a simple model illustrating conditions which may lead to the solution of iron in a groundwater. This figure is an oversimplification because it ignores the fact that iron and manganese are not generally found in the +II oxidation states, but rather as higher oxides.

Limitations on Solubility of Iron and Manganese

The concentrations of iron and manganese found in solution in natural waters are frequently limited by the solubility of their carbonates: siderite ($FeCO_3$) and rhodochrosite ($MnCO_3$). Waters of high alkalinity often, therefore, have lower iron and manganese contents than waters of low alkalinity. A simple calculation may serve to illustrate this phenomenon.

Effect of Alkalinity on Iron and Manganese Solubility

A rough comparison of the solubility of ferrous carbonate in waters having the same hydrogen ion concentration, $10^{-7}M$, but differing alkalinities, 50 and 500 mg/l $CaCO_3$ equivalent, can be obtained from the

Atmosphere:
78% nitrogen ($pN_2 = 0.78$)
21% oxygen ($pO_2 = 0.21$)
0.03% carbon dioxide ($pCO_2 = 0.0003$)
Ground Surface: covered by deposits of organic materials—grass, leaves, woody materials

Porous Soil: Percolation of water results in leaching of organic material from topsoil. In turn, bacterial oxidation of the organic material results in the depletion of oxygen and the production of carbon dioxide.

$$\text{Organic materials } (CH_2O) + O_2 \rightarrow CO_2 + H_2O$$

Groundwater Table

Groundwater: Continuing bacterial respiration results in the total depletion of dissolved oxygen. Gas analysis may yield the following:

$$pO_2 = 0.00$$
$$pCO_2 = 0.25$$
$$pCH_4 = 0.25$$
$$pN_2 = 0.50$$

The carbon dioxide then acts to dissolve carbonate-bearing minerals, including calcite, siderite, and rhodochrosite.

$$CaCO_{3(s)} + CO_2 + H_2O \rightarrow Ca^{++} + 2HCO_3^-$$
$$FeCO_{3(s)} + CO_2 + H_2O \rightarrow Fe^{++} + 2HCO_3^-$$
$$MnCO_{3(s)} + CO_2 + H_2O \rightarrow Mn^{++} + 2HCO_3^-$$

Fig. 2 Model of conditions leading to the solution of iron- and manganese-bearing minerals.

equilibrium expressions for the solution of ferrous carbonate and for the formation of carbonate ion.

$$\mathrm{FeCO_3}(s) \leftrightarrows \mathrm{Fe^{++}} + \mathrm{CO_3^{--}}$$
$$K_{\mathrm{FeCO_3}} = \mathrm{Fe^{++}CO_3^{--}} \tag{1}$$

$$\mathrm{HCO_3^-} \leftrightarrows \mathrm{H^+} + \mathrm{CO_3^{--}}$$
$$K_2 = \frac{\mathrm{H^+\,CO_3^{--}}}{\mathrm{HCO_3^-}} \tag{2}$$

Substituting Eq. (2) in Eq. (1) for $\mathrm{CO_3^{--}}$, we obtain:

$$\mathrm{Fe^{++}} = \frac{K_{\mathrm{FeCO_3}}}{K_2}\,\frac{\mathrm{H^+}}{\mathrm{HCO_3^-}} \approx \frac{\mathrm{H^+}}{\mathrm{HCO_3^-}} \tag{3}$$

Since most of the alkalinity is in the form of bicarbonate ion, the concentrations of bicarbonate are $10^{-3}M$ and $10^{-2}M$, respectively.

Therefore, when $\mathrm{HCO_3^-} = 10^{-3}M$, $\mathrm{H^+} = 10^{-7}M$

$$\mathrm{Fe^{++}} \approx 10^{-4}M \approx 5.5 \text{ mg/l Fe}$$

and when $\mathrm{HCO_3^-} = 10^{-2}M$, $\mathrm{H^+} = 10^{-7}M$

$$\mathrm{Fe^{++}} \approx 10^{-5}M \approx 0.55 \text{ mg/l Fe}$$

Equation (3) states that for a given pH the solubility of iron carbonate in natural waters is inversely proportional to the bicarbonate ion concentration or, for most waters, the alkalinity. The same is true of the solubility of all carbonates, including those of calcium and manganese.

In sulfate-bearing waters, bacterially mediated reduction can promote the formation of reduced sulfur species $\mathrm{S(-II)} = [\mathrm{H_2S}] + [\mathrm{HS^-}] + [\mathrm{S^{--}}]$. In the presence of concentrations of S(—II) as low as $10^{-5}M$ (0.37 mg/l $\mathrm{H_2S}$) the concentration of iron in aqueous solution may be limited by the solubility of pyrite ($\mathrm{FeS_2}$). This solubility restriction is so stringent that usually little or no iron or manganese is found in waters containing significant amounts of hydrogen sulfide.

Forms of Iron and Manganese in Solution in Natural Waters

When iron- and manganese-bearing minerals dissolve, they yield hydrated ions and hydroxide complexes according to the reactions shown in Table 11-2.

The sum of the aqueous ionic species having a particular oxidation state are designated Fe(II), Fe(III), Mn(II), Mn(IV), etc., to avoid enumeration of all of the individual ionic species present. For simplicity, the hydrated

TABLE 11-2 Protolysis and Polymerization Reactions of Iron and Manganese

---

Protolysis of Fe(II)

$$\mathrm{Fe(H_2O)_6^{++} \rightleftharpoons Fe(H_2O)_5OH^{+} + H^{+}}$$
$$\mathrm{Fe(H_2O)_5OH^{+} \rightleftharpoons Fe(H_2O)_4(OH)_{2(s)} + H^{+}}$$
$$\mathrm{Fe(H_2O)_4(OH)_{2(s)} \rightleftharpoons Fe(H_2O)_3(OH)_3^{-} + H^{+}}$$
$$\mathrm{Fe(II) = Fe^{++} + FeOH^{+} + Fe(OH)_3}$$

Protolysis of Mn(II)

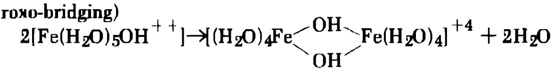
$$\mathrm{Mn(H_2O)_6^{++} \rightleftharpoons Mn(H_2O)_5OH^{+} + H^{+}}$$
$$\mathrm{Mn(H_2O)_5OH^{+} \rightleftharpoons Mn(H_2O)_4(OH)_{2(s)} + H^{+}}$$
$$\mathrm{Mn(H_2O)_4(OH)_{2(s)} \rightleftharpoons Mn(H_2O)_3(OH)_3 + H^{+}}$$
$$\mathrm{Mn(II) = Mn^{++} + MnOH^{+} + Mn(OH)_3^{-}}$$

Protolysis of Fe(III)

$$\mathrm{Fe(H_2O)_6^{+++} \rightleftharpoons Fe(H_2O)_5OH^{++} + H^{+}}$$
$$\mathrm{Fe(H_2O)_5OH^{++} \rightleftharpoons Fe(H_2O)_4(OH)_2^{+} + H^{+}}$$
$$\mathrm{Fe(H_2O)_4(OH)_2^{+} \rightleftharpoons Fe(H_2O)_3(OH)_{3(s)} + H^{+}}$$
$$\mathrm{Fe(H_2O)_3(OH)_{3(s)} \rightleftharpoons Fe(H_2O)_2(OH)_4^{-} + H^{+}}$$
$$\mathrm{Fe(III) = Fe^{+++} + FeOH^{++} + Fe(OH)_2^{+} + Fe(OH)_4^{-}}$$

Polymerization

Olation (hydroxo-bridging)



$$\mathrm{2[Fe(H_2O)_5OH^{++}] \rightarrow [(H_2O)_4Fe\overset{OH}{\underset{OH}{\rightleftharpoons}}Fe(H_2O)_4]^{+4} + 2H_2O}$$

(Dimer)

Oxolation (oxo-bridging)

$$\mathrm{2[Fe(H_2O)_5OH^{++}] \rightarrow [(H_2O)_5Fe - O - Fe(H_2O)_5]^{+4} + H_2O}$$

(Dimer)

---

ions are generally written without reference to the waters of hydration, their presence being understood. For iron and manganese up to six H_2O molecules are included in this inner coordination sphere.

In the pH range encountered in natural waters, the iron and manganese in solution consist primarily of hydrated ions, Fe^{++}, $FeOH^{+}$, Mn^{++}, and $MnOH^{+}$. While greatly limited in solubility at neutral pH, the aqueous ferric ions consist predominantly of $Fe(OH)_2^{+}$ and $Fe(OH)_4^{-}$.

The reactions shown in Table 11-2 show that the addition of ferrous, ferric, and manganese salts to water results in the release of hydrogen ion as protolysis proceeds. This accounts for the pH depletion frequently observed when salts of iron and aluminum are added to water as coagulants.

Polymerization and Precipitation

The hydrolyzed species of aquo-metal ions will condense to form higher polymers through hydroxo- and oxo-bridging. These processes are called "olation" and "oxolation," respectively. They lead first to the formation of polynuclear hydroxo complexes and, ultimately, to the formation of precipitates. Such reactions are extremely important in coagulation and precipitation processes in water treatment.

Inorganic and Organic Complexes

In addition to the hydroxide complexes other inorganic complexes may form where waters contain substantial amounts of bicarbonate, sulfate, phosphate, cyanide, or halides. The formation of such complexes would tend to increase the concentrations of iron and manganese found in solution. Most frequently, the concentrations of the complexing ligands present in natural waters are insufficient for important amounts of these complexes to form. However, in the case of Fe(III), the substitution of these other ligands for coordinated hydroxyl groups may have a marked influence on the behavior of the colloid formed, often enhancing its stability.

The formation of organic complexes and chelates may also increase the solubility of iron and manganese. Frequently, where difficulties in oxidation are encountered, "organic iron and manganese" are cited. Unfortunately, there is rarely any conclusive evidence that such complexes are present since there are currently no analytic techniques which will determine "organic iron" or "organic manganese." There is no question, however, that stable solutions or colloidal dispersions of iron and manganese can be prepared by the addition of organic acids.

Ferric iron forms more stable organic complexes than ferrous iron which, in turn, forms complexes of greater stability than Mn(II). While Fe(II) can form complexes with alcohols, esters, diketones, and aldehydes Fe(III) can form complexes, often colored, with these as well as with ethers and phenols. In natural waters, however, the organic substances found are extracts from decaying vegetation, often referred to as "humic" and "fulvic" acids. Iron (III) is believed to form chelates with these acids, which are frequently colored, through coordination with the hydroxyl and carboxyl functional groups. There is a question as to whether these chelates are soluble in neutral solutions, however. It is probable that at the pH values encountered in natural waters these complexes are insoluble but highly dispersed.[2]

The natural color of water may frequently be caused by these highly stabilized colloidal dispersions of iron.

Since the coordination between Mn(IV) and OH^- is stronger than that between Fe(III) and OH^-, Mn(IV) does not readily form complexes with either organic or inorganic ligands in natural waters.

Equilibrium Relations Governing Iron and Manganese Solubility

Overall, the solubility of iron and manganese in carbonate-bearing waters devoid of both oxygen and sulfides can be approximately computed from the equilibria presented in Table 11-3.

For a given pH and total carbonic acid concentration (C_T), the solubility of iron and manganese in water is computed using the equilibrium expressions for the equations listed and setting $\mathrm{Fe(II)} = \mathrm{Fe}^{++} + \mathrm{FeOH}^{+}$ and $\mathrm{Mn(II)} = \mathrm{Mn}^{++} + \mathrm{MnOH}^{+}$. For groundwaters, where temperatures are frequently close to 15 °C and ionic strengths about $10^{-2}M$, the equilibrium constants must be corrected for temperature. Moreover, the activity coefficients must be computed for each of the ionic species considered in the equilibria.

TABLE 11-3 Equilibria Governing Iron and Manganese Solubility

Fe(II) Solubility and Hydrolysis Reaction	$-\log K_{(25°\mathrm{C})}$
1. $\mathrm{Fe(OH)}_{2(s)} \rightleftharpoons \mathrm{Fe}^{++} + 2\mathrm{OH}^{-}$	15.1
2. $\mathrm{FeCO}_{3(s)} \rightleftharpoons \mathrm{Fe}^{++} + \mathrm{CO}_3^{--}$	10.7
3. $\mathrm{Fe}^{++} + \mathrm{H_2O} \rightleftharpoons \mathrm{FeOH}^{+} + \mathrm{H}^{+}$	8.3
Mn(II) Solubility and Hydrolysis Reaction	
4. $\mathrm{Mn(OH)}_{2(s)} \rightleftharpoons \mathrm{Mn}^{++} + 2\mathrm{OH}^{-}$	13.0
5. $\mathrm{MnCO}_{3(s)} \rightleftharpoons \mathrm{Mn}^{++} + \mathrm{CO}_3^{--}$	10.4
6. $\mathrm{Mn}^{++} + \mathrm{H_2O} \rightleftharpoons \mathrm{MnOH}^{+} + \mathrm{H}^{+}$	10.6
Protolysis of Carbonic Acid	
7. $\mathrm{H_2CO_3} \rightleftharpoons \mathrm{HCO_3}^{-} + \mathrm{H}^{+}$	6.4
8. $\mathrm{HCO_3}^{-} \rightleftharpoons \mathrm{CO_3}^{--} + \mathrm{H}^{+}$	10.3
Ion Product of Water	
9. $\mathrm{H_2O} \rightleftharpoons \mathrm{H}^{+} + \mathrm{OH}^{-}$	14.0

HISTORY OF THE PRACTICE OF IRON REMOVAL

Iron and manganese removal is one of the most recent of waterworks practices. Less than a century ago, in 1874, the first iron-removal plant was constructed at Charlottenburg, Germany. In 1893, the first iron-removal plant in the United States was placed in operation at Atlantic Highlands, New Jersey. The earliest plants employed aeration and filtration, sometimes supplemented by the addition of lime, to treat groundwaters. The same method of treatment predominates today.

The first plant to remove manganese along with iron was completed in 1889 in Zutphen, Holland. However, little real attention was paid to manganese removal until the "Breslau calamity" in 1914 when the manganese content of the well water from Breslau, Germany, suddenly increased precipitously to 220 mg/l. Simultaneously, the iron concentration increased to 440 mg/l.

By 1941 there were a reported 598 iron and manganese removal plants in the United States. The great majority served small communities and the total pumpage was only 220 mgd or an average of 370,000 gpd per plant. By 1958, approximately 1,340 water-treatment plants, roughly 14 per cent of the total in the United States, included processes for the removal of iron and manganese.

METHODS OF THE REMOVAL OF IRON AND MANGANESE

There are three general methods used for the control of iron and manganese in public water supplies at the present time. The primary method involves precipitation followed by filtration. The second method involves ion exchange, and the third method involves stabilization of the iron and manganese in suspension using dispersing agents to prevent the deposition of these metals. The third method is generally employed where the municipal water is not treated by filtration, and the iron and manganese concentrations are less than 1.0 mg/l.

More specifically, the treatment processes employed in the control of iron and manganese deposition include:

1. Precipitation and filtration
    - *a.* Aeration, detention, filtration (with supplementary chlorination and/or the addition of lime)
    - *b.* Oxidation by potassium permanganate, chlorine, or chlorine dioxide followed by filtration
    - *c.* Calcined magnesite—diatomaceous earth filtration
2. Ion exchange
    - *a.* Ion-exchange (zeolite) softening
    - *b.* The manganese-zeolite process
3. Stabilization with polyphosphates

Description of Methods

In water-treatment practice, the great majority of iron- and manganese-removal plants in the United States employ aeration, detention (or sedimentation), and filtration. In many instances, chlorine is added following aeration to aid in oxidation. Where the pH is too low for rapid oxidation, lime is added.

Although in the absence of oxygen it is possible to remove iron and manganese on zeolite exchange media, this practice is restricted to individual water supplies in which iron and manganese concentrations are low, generally less than 0.5 mg/l, because accumulations of precipitates of these metals may cause the exchange medium to lose its exchange capacity. In municipal water-treatment practice, it is more common to remove iron and manganese by aeration and filtration prior to utilizing ion exchange for softening. Iron and manganese removal is, of course, incidental to softening by precipitation with lime and soda.

Strong oxidants, such as chlorine, chlorine dioxide, and potassium permanganate are employed chiefly where waters contain manganese. Breakpoint chlorination is found to result in slow precipitation of hydrated manganese dioxide unless a pH of 8.0 is exceeded. Oxidation by chlorine dioxide is reported to be somewhat faster. However, in practice the pH may have to be maintained above 8.5 to obtain effective manganese removal.

Potassium permanganate will oxidize manganous ion to manganese dioxide rapidly (within 5 min) over a broad pH range. The dosage of $KMnO_4$ required for the oxidation decreases with increasing pH. This may be due to increased adsorption of Mn(II) by MnO_2 at higher pH. Nevertheless, unless a slightly alkaline pH of 7.5 to 8.0 is maintained, difficulties may be encountered in the coagulation or filtration of the colloidal MnO_2 formed. Chlorine may be applied prior to permanganate to oxidize some of the reducing agents present, such as ferrous iron. These reductants would otherwise react to consume the more costly oxidant, permanganate.

While less common, the removal of iron and manganese on continuously regenerated permanganate greensand filters is practiced and is reportedly successful. Aeration is avoided as potassium permanganate is continuously added to the raw groundwater prior to passage through a bed of zeolite (greensand) exchange medium. The permanganate oxidizes the iron and manganese so that the exchange medium becomes coated with the oxidation products. Where the amount of precipitate is large, a layer of crushed anthracite coal on top of the exchange medium is sometimes used to prolong filter runs. The hydrous oxides of iron and manganese deposited on the exchange medium have a large sorption capacity for Fe(II) and Mn(II). This capacity makes it possible to operate the filter on an intermittent basis, regenerating with $KMnO_4$ after the exchange capacity is exhausted, to oxidize the adsorbed Fe(II) and Mn(II).

A method of iron and manganese removal recently finding application employs calcined magnesite and diatomaceous earth filtration. Calcined magnesite (MgO) and diatomaceous earth are fed to a rapid-mix tank which provides 5 to 10 min of contact during which Fe(II) and Mn(II) are oxidized in contact with the MgO. Where manganese is to be removed, $KMnO_4$ is used as the oxidizing agent. Thereafter, the water is filtered through a diatomaceous-earth filter. An advantage of this system is that the filter medium is discarded after each filtration cycle, thereby avoiding any accumulation of precipitates or bacterial growths on the filter medium.

Stabilization

The alternative to iron and manganese removal is stabilization or dispersion. Sodium hexametaphosphates at dosages of 5 mg per mg of Fe plus Mn have been used for this purpose. While this treatment will stabilize iron and manganese in suspension, it reportedly is not suitable where metal concentrations of 1 mg/l are exceeded. Moreover, when the water is heated, the polyphosphate will revert to orthophosphate and lose its dispersing properties. The application of the polyphosphate must take place prior to aeration or chlorination because the polyphosphates do not effectively stabilize precipitated ferric hydroxide.

Polyphosphate dosages are limited to less than 10 mg/l, because the availability of phosphorus may stimulate bacterial growths in distribution systems. Where polyphosphates are used to maintain colloidal dispersions of iron and manganese or to prevent calcium carbonate deposition, chlorine residuals must be sufficient to control bacterial slime growths.

BACTERIALLY MEDIATED CHEMICAL TRANSFORMATIONS OF IRON AND MANGANESE

The growth of microorganisms associated with iron and manganese can cause severe problems in wells, water distribution systems, and reservoirs. Slime thicknesses of up to several centimeters have been observed on the walls of mains. These accumulations, which consist of deposits of hydrous iron and manganese oxides plus bacterial masses, can result in marked decreases in pipeline carrying capacities, increased pumping heads, the consumption of chlorine residuals, and the depletion of dissolved oxygen in the water. The sloughing of these accumulations leads to excessive turbidities and complaints of "red" and "black" water. Frequently, the decomposition of these accumulations results in the production of objectionable tastes and odors.

Iron and Manganese Bacteria

Formerly, all organisms which were found in the presence of oxidized deposits of iron and manganese were loosely referred to as "iron and manganese bacteria," or, more frequently, "iron bacteria." It was thought that all organisms which were capable of depositing iron were capable of deriving energy from the oxidation of Fe(II) to Fe(III). These organisms are generally filamentous, aerobic, and found chiefly in waters that contain significant amounts of iron and manganese in solution. They may accumulate very substantial amounts of precipitated iron and manganese around their cells or within their sheaths. The accumulated precipitates may even mask their presence. As a result, *Standard Methods,* 12th Edition, has defined iron bacteria as "those bacteria capable of withdrawing iron present in their aqueous habitat and of depositing it in the form of ferric hydroxide on or in the mucilaginous sections." While this definition may be satisfactory for engineering purposes, the more precise definition of iron bacteria used by microbiologists refers to those chemoautotrophs which are capable of oxidizing iron as their sole energy source.

Nonspecific Bacteria

While the iron bacteria are capable of accelerating the oxidation of ferrous iron to form hydrous ferric oxides, other heterotrophic or nonspecific bacteria can also have important effects on the equilibrium conditions which affect the solution or deposition of iron and manganese. Perhaps the two most important changes that might be caused by such organisms in the presence of traces of organic compounds in water are the consumption of oxygen and the production of carbon dioxide. The depletion of dissolved oxygen may be a prelude to severe reducing conditions, while the increase in the carbon dioxide content will lower the pH. Both influences would tend to result in the solution of deposits of iron and manganese.

The action of nitrifying bacteria can result in oxygen depletion and increased nitrite and nitrate concentrations. Thereafter, under anaerobic conditions, sulfate-reducing bacteria may produce hydrogen sulfide. This reducing agent is capable of reducing ferric and manganic salts and, at the same time, of precipitating ferrous and manganous sulfides and disulfides.

In cases where iron and manganese are stabilized by organic materials, the bacterial oxidation of the organic matter may result in destabilization and deposition of the precipitates. On the whole, the growth of virtually all of the organisms, autotrophic as well as heterotrophic, appears to be stimulated by the presence of dissolved organic matter.

Clark[3] has suggested the classification of bacteria associated with iron shown in Table 11-4. Of those listed, only *Ferribacillus* and *Gallionella* are believed to be true iron bacteria. *Crenothrix* and *Leptothrix* may be facultative autotrophs.

Of those listed, *Leptothrix*, *Gallionella*, and *Crenothrix* are found most frequently in water supplies. The *Gallionella* often predominates in waters low in organic matter, while the others predominate in waters higher in organic content. It has been suggested that ammonium ion may serve as the nitrogen source for these bacteria.

OXIDATION AND PRECIPITATION OF IRON AND MANGANESE

Iron and manganese can be precipitated as carbonates in carbonate-bearing waters by addition of lime or soda ash. These precipitations take place under anaerobic conditions. Figure 3 shows plots of the solubility of Fe(II) and Mn(II) in water having a concentration of total carbonic species,

$$C_T = H_2CO_3 + HCO_3^- + CO_3^{--} = 10^{-3}M$$

TABLE 11–4 Classification of Bacteria Associated with Iron[3]

Bacterial classification	Characteristics
Chlamydobacteriales	Order of unbranched, filamentous sheath-forming bacteria. Sheath may be of organic matter alone or impregnated with iron
Sphaerotilus	Rod- or oval-shaped cells in colorless sheath. Widely distributed in waters containing relative abundance of organic matter
Leptothrix	Cylindrical cells in filamentous sheath. Cells may escape from sheath and leave empty tubes of ferric hydrate. Commonly found in waterworks
Crenothrix	Cylindrical to spherical cells in unbranched sheath which thickens and darkens with time. Commonly found in wells and mains with *Gallionella*
Pseudomonadales Caulobacteriaceae	Order of polarly flagellated bacteria capable of attachment to objects by a stalk
Gallionella	Small, asymmetrical, concave rods which secrete a flat, twisted ribbon of hydrous ferric oxide to one side. Organism is thought to be a true autotroph. Commonly found in iron-bearing waters
Pseudomonadales Siderocapsaceae	Group of polarly flagellated discrete cells
Siderocapsa	Coccoid cells or short rods composed of about 10 cells per colony surrounded by a mucoid capsule. Not readily detected because of small size compared to filamentous bacteria
Ferribacterium	Little information available
Ferribacillus	Unicellular bacteria, thought to be true autotrophs

Examination of the plots indicates that under these conditions ferrous and manganous carbonate may be expected to precipitate almost completely at pH values above 8 and 8.5, respectively. Precipitation of ferrous and manganous hydroxides requires that the pH be increased to about 11. Mixtures of these precipitates may be formed during lime-soda softening.

Most frequently for the precipitation of iron and manganese, advantage is taken of the fact that ferric hydroxide and manganese dioxide are far less soluble than the hydroxides and carbonates of Fe(II) and Mn(II). Therefore, Fe(II) and Mn(II) are oxidized, most commonly, by oxygen, chlorine, potassium permanganate, or, in rare cases, by ozone. Figure 3 indicates that oxidation of Fe(II) to Fe(III) will greatly reduce the solubility of iron over a very broad pH range, 4 to 12.

Kinetics of Oxidation

1. *Iron.* The rate of oxidation of Fe(II) by oxygen (oxygenation) is slow under conditions of low pH as shown in Fig. 4. In such cases, pH is increased by stripping carbon dioxide or adding lime. Alternately, the rate

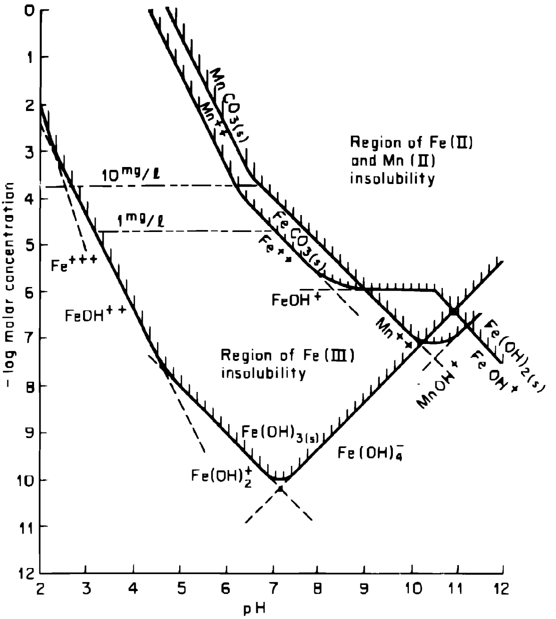
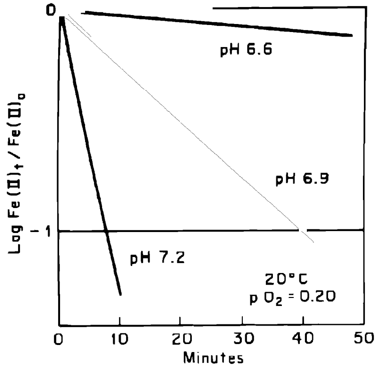


Fig. 3 Solubility of Fe(II), Mn(II), and Fe(III) in carbonate-bearing water ($C_T = 10^{-3}M$). (*After Stumm.*[4])

of oxygenation may be increased by the use of a catalyst. In the practice of iron removal, contact aerators and contact filters have long been used in an effort to accelerate iron oxidation. The accumulations of deposited iron and bacteria on coke, rocks, and sand grains were presumed to act as the catalysts.

Measurements of the rates of Fe(II) oxidation in natural waters are beset by analytic problems because of the difficulty in determining ferrous ion in the presence of reducing agents and incipient precipitates of ferric oxide. However, measurements of the rate of conversion of Fe(II) to a filterable form in groundwaters indicate that the rates of iron precipitation and agglomeration are slower than those indicated in Fig. 4.[6] It has been suggested that the inhibition of iron oxidation may be the result of the reduction of Fe(III) by organic substances which behave in a manner similar to tannic, gallic, or ascorbic acids.[7] Until all this organic material is oxidized, the rates of iron oxidation may be inhibited and the precipitate formed may be stabilized. It is possible, therefore, that the widespread chlorination of many iron-bearing waters results in the oxidation of the organic matter and other reducing agents present rather than in the direct oxidation of Fe(II).



Rate law for Fe(II) oxygenation:

$$-\frac{d[Fe(II)]}{dt} = k[Fe(II)][O_2][OH^-]^2$$

Fig. 4 Oxygenation of Fe(II). (*After Stumm and Lee.*[5])

2. *Manganese.* Since the rate of oxygenation of Mn(II) is relatively slow at pH values below 9.5, as shown in Fig. 5, the effect of catalysis by deposits of manganese dioxide has long been felt to be particularly important. However, Morgan[8] has shown that a major effect of MnO_2 is to adsorb Mn^{++}, thereby effecting its removal during filtration. Thereafter, the adsorbed manganese continues to oxidize at a slow rate. The suggested reaction steps in the oxygenation of Mn(II) are:

$$Mn(II) + \tfrac{1}{2}O_2 \xrightarrow{\text{slow}} MnO_{2(s)}$$

$$Mn(II) + MnO_{2(s)} \xrightarrow{\text{fast}} Mn(II) \cdot MnO_{2(s)}$$

$$Mn(II) \cdot MnO_{2(s)} + \tfrac{1}{2}O_2 \xrightarrow{\text{slow}} 2MnO_{2(s)}$$

Other oxidizing agents commonly used for iron and manganese oxidation are chlorine and potassium permanganate. These oxidants are frequently used where reducing agents may include nitrite, hydrogen sulfide, and organic compounds. Relatively little information is available as to the kinetics of oxidation where oxidants other than oxygen are used.

Sorption of Fe(II) and Mn(II)

Sorption reportedly plays a significant role in the removal of iron and manganese from solution. Precipitates of hydrous oxides of Fe(III) and manganese dioxide both have high sorption capacities for Fe(II) and Mn(II). This phenomenon may account for the removal of iron and manganese on contact filters as well as within filters where the filter medium is coated with precipitates. A period of filter "ageing" is required for the deposition of the precipitate to take place.

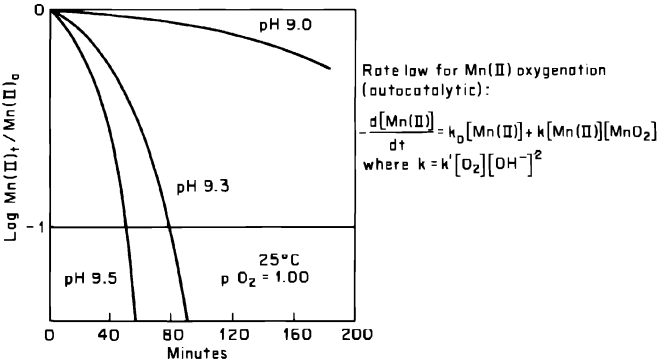
Zeolites and other materials treated with solutions of Mn^{++} and MnO_4^- become coated with MnO_2. This coating is then capable of sorbing Fe(II) and Mn(II). Periodically, as the sorption capacity is exhausted, the sorbed Fe(II) and Mn(II) can be oxidized by the application of potassium permanganate.

Precipitation of Fe(II) by MgO

The addition of calcined magnesite (MgO) to waters of low pH can promote the rapid oxidation of Fe(II) without markedly increasing the pH of the treated water. One possible explanation for the observed phenomenon is that the slow solution of the MgO during a 10-min period of intense agitation results in the transient formation of pinpoint regions of high pH. It is likely that the oxidation takes place in those regions close to the surface of the MgO particles, owing to the high localized hydroxyl concentration.

THE PRACTICE OF IRON AND MANGANESE REMOVAL

The most common method of removing iron and manganese from municipal water supplies involves three basic steps: aeration, detention, and filtration. Aeration serves a variety of purposes. Primarily, it introduces oxygen into solution. In addition, it serves to reduce the carbon dioxide content of most groundwaters, thereby increasing the pH. Methane, if present, will be readily removed by aeration, and hydrogen sulfide will be partially removed. Finally, the aeration step may also be used to provide contact between the water and the oxidized precipitates attached to a contact surface. The contact aerator, which generally contains trays of coke, limestone, traprock, pyrolusite, or wooden slats, is most commonly used for aeration in iron- and manganese-removal practice.



Rate law for Mn(II) oxygenation (autocatalytic):

$$-\frac{d[\mathrm{Mn(II)}]}{dt} = k_0[\mathrm{Mn(II)}] + k[\mathrm{Mn(II)}][\mathrm{MnO_2}]$$

where $k = k'[\mathrm{O_2}][\mathrm{OH^-}]^2$

Fig. 5 Removal of Mn(II) by oxygenation. (*After Morgan.*[8])

The precipitation and agglomeration of iron and manganese is not instantaneous. Even where strong oxidants such as chlorine and permanganate are used, detention must be provided following aeration to allow time both for oxidation to proceed and for oxidized iron and manganese to agglomerate to a filterable size.

Sedimentation is rarely specifically provided unless the concentration of iron and manganese in the raw water is quite high (>10 mg/l). Little sedimentation occurs in most detention tanks. Instead, the detention tanks may be considered to be quiescent reaction basins. Up to this time little consideration has been given to stirring of these reaction basins, although in many cases the contact provided thereby may be beneficial in promoting agglomeration and adsorption.

In iron- and manganese-removal practice, filtration is frequently provided by pressurized rapid-sand filters without surface or air wash. The sand used is normally somewhat coarser than that used for waters which have been coagulated. Since little settling of precipitates will occur in the reaction basin, most of the iron and manganese present in the raw water are present in the filter influent. Frequently, mud balls form in the pressurized filters due to deposits of iron, manganese, and calcium which cement the sand grains together. This condition often goes undetected unless the filter is opened and probed frequently.

In many plants where iron and manganese consistently pass through the filter units, prechlorination is practiced as a remedial measure.

Survey of Performance of Iron-removal Plants

A survey of the performance of 31 plants practicing iron removal in Illinois was made in 1960.[9] The results of this survey provide some indication of the effectiveness of aeration and filtration for iron removal.

Aeration, generally by coke tray aerators, was found to be effective in introducing oxygen into all the waters. During aeration, the pH increased by an average of 0.3 unit so that the pH of the aerated waters ranged between 7.0 and 8.0.

Although 1 hr of detention was normally provided following aeration, frequently a large fraction of the iron in the filter influent appeared still to be in the ferrous form. Much of this unoxidized iron also appeared in the filter effluent, indicating that complete oxidation might have resulted in more complete iron removal.

An unexpected result of the survey was the observation that oxygen was frequently depleted, often almost totally, in the filter effluent. This was accompanied by an increase in the nitrate concentration of the filtered water.

Overall, the survey indicated that at 18 of the 31 plants surveyed the finished water contained iron in excess of 0.3 mg/l, while at 9 plants, the iron exceeded 1.0 mg/l.

Figure 6 illustrates conditions which might be considered typical of a treatment plant in Illinois which was removing iron effectively. The ferrous iron is almost completely oxidized. The ferric iron is removed by filtration. However, total bacterial plate counts may increase, particularly after filtration.

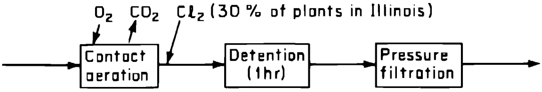
Possible Design Deficiencies

The survey indicated that design deficiencies may exist when insufficient reaction time is provided for the complete oxidation and agglomeration of iron and manganese. The amount of time required apparently must be determined by measuring the kinetics of precipitation for each individual water.

During each filter cycle a crust several inches thick will frequently form at the surface of filters due to the binding together of sand grains in a matrix of oxidized iron and manganese plus calcium carbonate. During backwash, this surface crust will break, and the fragments will settle to the bottom of the filter bed following backwash. Mechanical methods of filter cleaning, such as surface wash, can retard such mud ball formation.

BIOCHEMICAL ASPECTS OF FILTRATION

Bacterial growths in rapid-sand filters may mediate a variety of chemical changes in the water being filtered. The amount of organic matter available in natural waters for the establishment of bacterial growths in filters generally is not large in terms of concentration. However, considering the large volume of water filtered, the total amount of organic material entering a filter may often be sufficient to support a substantial population of heterotrophic bacteria. Moreover, autotrophic bacteria can utilize the carbonate system as their carbon source.



D.O.	0.0	8.0	8.0	0.2
Fe(II)	3.0	1.5	0.1	0.1
Fe(III)	0.0	1.5	3.0	0.0
pH	7.2	7.6	7.6	7.4
NH_4^+	1.0	1.0	1.0	0.2
Bacteria (20° C, total plate count)	1,000/ml	1,000/ml	2,000/ml	20,000/ml

Fig. 6 Typical iron-removal plant performance.

Of the latter group, the nitrifying organisms may be particularly influential. These ubiquitous organisms derive energy for their metabolism from the oxidation of ammonium ion and, in doing so, utilize about 4.5 mg of oxygen per mg of ammonia nitrogen. Therefore, where the ammonia nitrogen concentration of raw water is on the order of 2 mg/l, nitrification may lead to total oxygen depletion during filtration. The resulting anaerobic conditions in the filter may be a first step toward a return to solution of the iron and manganese deposited in the filter. The application of potassium permanganate following backwash has been shown to be successful in inhibiting the process of nitrification for up to a month.[10] More frequent applications of chlorine at dosages of 1,000 mg/l may accomplish the same results.

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12

Fluorides in Water

By F. J. MAIER

The controversy accompanying the adoption of fluoridation in many communities often directly involves the water plant superintendent and his employees. The superintendent is frequently considered the outstanding authority on water fluoridation in his community because fluoridation is another aspect of water treatment.

Over 25 years of extensive experience has proved the adjustment of the fluoride content of community water supplies to be effective, safe, and practical. Fluoridation has been shown to reduce dental decay among children by two-thirds. No known deleterious effects have been noted in anyone drinking fluoridated water. Any community choosing to fluoridate its water supply has been able to do so with accuracy and with a better return on its investment than any other public health measure. The average cost is only about 10 cents per person per year.

This proven public health measure is being considered seriously for every community where water supply is deficient in fluoride because in the United States today:

Over 90 per cent of 7-year-old children have at least one decayed tooth.

Sixteen-year-olds have an average of seven carious teeth.

The average adult has lost one-half his teeth by the age of 40.

Over 20 million persons have lost all their teeth.

The AWWA Board of Directors adopted on April 29, 1951, and reaffirmed on June 17, 1962, and January 25, 1970, a policy statement on fluoridation of public water supplies, as follows: "In communities where a strong public demand has developed and the procedure has the full approval of the local medical and dental societies, the local and state health authorities, and others responsible for the communal health, water departments or companies may properly participate in a program of fluoridation of public water supplies."

This position is based on the fact that fluoridation is a public health program in which AWWA believes that water utility operators might legitimately participate after the program has received the approval of local and state health authorities and, of course, the approval of the town council.

HISTORY

Reduction in dental caries is not the only effect of fluorides on dental health. In 1901, a U.S. Public Health Service physician stationed in Naples, Italy, wrote that the black teeth he observed in his examination of emigrants from a nearby region were popularly believed to have been caused by using water charged with volcanic fumes. It was later determined that the water supply contained extremely high amounts of fluorides and that everyone drinking it was afflicted with discolored (or "mottled") teeth.

In its mildest form this condition is characterized by very slight, opaque, whitish areas on some of the posterior teeth. As the defect becomes more severe, the mottling is more widespread, and changes in color range from shades of gray to black. In the most severe cases, gross calcification defects occur, resulting in pitting of the enamel. In some of the latter cases, the teeth are subject to such severe attrition that they wear down to the gum line, and complete dentures must be obtained.

Several observers reported such defects among children in Italy and England. In 1916 Dr. Frederick S. McKay, a practicing dentist, reported that many of his patients in Colorado Springs, Colorado, had this defect. Later, by studying the many degrees of severity of the condition, he arrived at the conclusion that it was caused by an undetermined substance in the drinking water. McKay recommended that the water supply of Oakley, Idaho, be changed because of the high incidence of such dental defects among the children there. The supply was changed in 1925 to a nearby spring which had been used by a few other children whose teeth were not discolored. McKay's conclusion was further verified in Bauxite, Arkansas. Here, there had been a change in water supplies in 1909. Prior to that year there was no dental discoloration; however, after the water supply was changed children reared on the water developed "mottled" enamel in varying degrees. In addition, those whose tooth enamel had developed elsewhere and who had then moved to Bauxite had no discoloration.

An interesting sidelight on Dr. McKay's conviction regarding the role of water supplies was his plea to waterworks experts for help in interpreting water analyses. In 1926 he reviewed his accumulated evidence leading to the implication of water supplies and ruled out any connection between the calcium or iron content of water and the incidence of dental discoloration.

Replies solicited from prominent water-treatment experts typified the opinion of most observers as to the probable causes of mottling. Theories as to the ingredient in water which might contribute to the cause were founded on manganese, acidity, pH, hardness, organic material, unbalanced diet, and the effect of the mother's diet on the dental health of the child. A most significant reply came from Frank Hannan, the chemist at the Toronto, Ontario, filtration plant. Mr. Hannan wrote in part:

> Since the enamel is essentially mineral in composition and the water definitely incriminated, the mineral content of the water seems the probable source of the trouble. Of the mineral elements at present known to be common to both water and enamel, the chief ones are calcium, phosphorus, and fluorine. For our intake of phosphorus, we are independent of the small proportion found in water; the same can be asserted of calcium with perhaps a shade less certainty, a dietary deficiency in this element being not altogether unusual. But when we consider fluorine, all is at present shrouded in obscurity. The detection and estimation of small traces of fluorine are tedious and troublesome and quite outside the province of the ordinary water works chemist who has to handle many thousands of samples in a year. The French chemist Gautier found fluorine practically universally present in water. That it cannot exist there in more than traces is fortunately secured to us by the low solubility product of calcium fluoride, fluorine in sizable doses being a rather powerful poison. The U.S. Public Health Service seems indicated to handle a many-sided, time-consuming research of this kind. Should the incriminated waters prove to be all alike fluorine free, the case for fluorine deficiency will become strong.

Unfortunately, Dr. McKay dismissed Mr. Hannan's suggestion with "None of the elements mentioned by Mr. Hannan seem to have any direct possibility of producing a decalcification."

Collaborating with other investigators in 1928, Dr. McKay stated:

> My testimony has been supplemented by that of others, who report that these mottled enamel cases in the various districts are singularly free of caries. . . . The great majority of cavities consisted of small pit and fissure lesions in the molars and seldom did caries extend beyond that stage. In this respect the behavior of dental caries in the mouths of these children is distinctly different to that which usually occurs.

Several more years were to elapse before the cause of mottled enamel was discovered. Almost simultaneously, three different groups of scientists working independently with entirely different tools and methods—and at such widely separated places as Pennsylvania, Arizona, and North Africa—defined the causal agent.

A. W. Petrey, a chemist with the Aluminum Company of America at Pittsburgh, noticed the calcium fluoride band in a spectroscopic examination for aluminum in a water sample from Bauxite, Arkansas. The chief chemist of these laboratories, H. V. Churchill, reported in 1931 that similar examinations of water samples from areas where mottled enamel was endemic invariably showed the presence of fluorides.

At almost the same time, Drs. H. V. Smith, M. C. Smith, and E. M. Lantz at Arizona reported the cause of mottling by duplicating the condition in rats by feeding concentrated naturally fluoridated water and comparing the results with the mottling observed when a diet high in fluorides was used. Also during 1931, H. Velu in North Africa showed that the condition could be produced in animals who were fed waters saturated with natural phosphates from Algiers and Morocco, the lesions being identical to those produced by feeding rats a high-fluoride diet.

Dr. Churchill concluded that endemic regions had waters containing 2 ppm or more fluoride while those areas without mottling had water supplies with less than 1.0 ppm. This division of fluoride waters was confirmed by the Smiths in Arizona, who reported that water sources from nonendemic areas contained less than 0.72 ppm fluoride.

Soon after this Dr. H. Trendley Dean of the U.S. Public Health Service began his carefully prepared and executed epidemiological investigations. He confirmed that many localities have water supplies containing fluoride. Areas with the largest number of such supplies containing the highest levels of fluorides include those states running from North Dakota to Texas, those along the Mexican border, and Illinois, Indiana, Ohio, and Virginia. Similar supplies are found in the British West Indies, China, Holland, Italy, Mexico, North Africa, South America, Spain, and India. The areas in the United States known to contain supplies having more than 0.7 ppm fluoride are shown in Fig. 1. There are over 1,200 known communities in the United States comprising 4.1 million people using water containing fluorides in excess of the "optimum." In order to avoid the inevitable disfiguring fluorosis, these places could either change their supplies, or install a water plant designed to remove the excessive fluorides.

Through his observation of thousands of children in communities with varying fluoride levels, Dr. Dean established what he termed a "mottled-enamel index"—a numerical method for measuring the severity of fluorosis. With this index he was able to establish the fluoride level below which the use of such water contributed no significant discoloration. This level in the latitude of Chicago was about 1.0 ppm.

Many investigators, including Dr. McKay, had observed during the 1920s

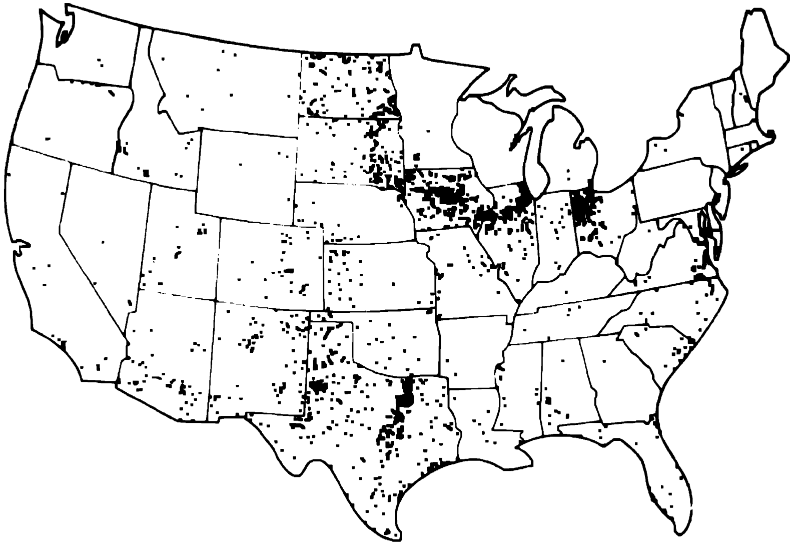

Fig. 1 Communities using naturally fluoridated water containing 0.7 ppm or more fluoride. (*USPHS.*)

that there was possibly less decay among children whose teeth were afflicted with "mottling." In order to confirm this, Dr. Dean examined 7,257 children in 21 cities with water supplies containing varying fluoride levels. A graph (Fig. 2) prepared from these data and Table 12-1 show the remarkable relationships between waterborne fluorides and fluorosis and caries incidence. Three facts were obvious from Dr. Dean's figures:

1. When the fluoride level exceeds about 1.5 ppm, any further increase does not significantly decrease the decayed, missing, and filled (DMF index) tooth incidence, but does increase the occurrence and severity of mottling.
2. At a fluoride level of about 1.0 ppm the optimum occurs—maximum reduction in caries with no aesthetically significant mottling. At this level he found the DMF rates were reduced by 60 per cent among the 12- to 14-year-old children.
3. At fluoride levels below 1.0 ppm some benefits occur, but caries reduction is not as great and gradually decreases as the fluoride levels decrease until, as zero fluoride is approached, no observable improvement occurs.

With this knowledge it was inevitable that fluorides would be added to a water supply and the effects measured. The interruption caused by World War II delayed such studies until 1945, when three cities (Grand Rapids, Michigan; Newburgh, New York; and Brantford, Ontario) instituted programs of fluoridating their water supplies.

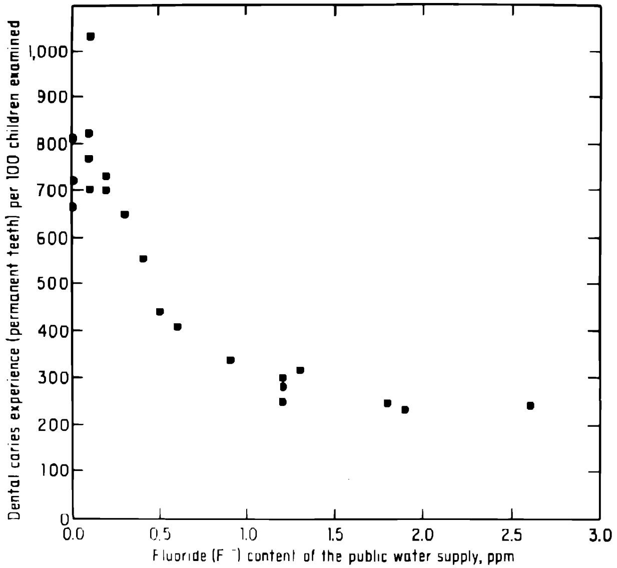

Fig. 2 Relation between the amount of dental caries (permanent teeth) observed in 7,257 selected 12- to 14-year-old white school children of 21 cities of four states and the fluoride (F^-) content of public water supply.

INITIAL INSTALLATIONS AND RESULTS

The demonstrations were intended to show the similarity of fluoridation of a public water supply with those containing natural fluorides. The projects had to be carefully controlled. Two principles were used, not only at the three initial projects (Grand Rapids, Michigan; Newburgh, New York; and Brantford, Ontario) but at almost all other study projects in the world:

1. All children examined had lived in the community continuously (absences up to 30 days per year permitted) and had used the local public water supply during this time.

2. Examinations were made to reveal for each child the number of decayed, unfilled teeth, the number of filled teeth, and those which should have been extracted because of extensive tooth decay or other causes. This latter measure provided data for formulating a DMF rate which was used to compare results not only among the children in the same community, but with other communities throughout the world.

The methods of making dental examinations were more or less standard in all the early fluoridation studies. Even though the examiners at the three initial demonstrations were different individuals, their results, shown in Fig. 3, were remarkably similar.

Each of these studies included a similar examination of children in a control city with parallel characteristics except for the fluoride content of the water supply. These places, with their original fluoride content (in parts per million), were: (1) Grand Rapids, Michigan (0.15 raised to 1.0); Muskegon, Michigan (0.15); Aurora, Illinois (1.2); (2) Newburgh, New York (0.1 raised to 1.1); Kingston, New York (0.1); (3) Brantford, Ontario (0.1 raised to 1.0); Sarnia, Ontario (0.1); Stratford, Ontario (1.2).

Other studies in the United States where results with the base lines established within the studied areas (no control city used) were compared were: Marshall, Texas; Evanston, Illinois; Sheboygan, Wisconsin; Ottawa, Kansas; Lewiston, Idaho; and Southbury School, Southbury, Connecticut.

As a result of these programs, it was possible to follow the progress of fluoridation results very closely. A typical report of this progress is shown in Fig. 4, which includes the base-line examinations at both Grand Rapids and at Aurora.

From these results several conclusions can be drawn:

1. Each successive yearly examination revealed progressive improvement in the reduction of decayed, missing, and filled teeth.
2. The younger age groups showed the earliest improvement and, at any given time, the greatest DMF rate reduction (Fig. 5).
3. As the duration of the fluoridation procedure approached the age of the children, the DMF rates approached the rate of Aurora (where the water supply naturally contains 1.2 ppm fluoride), which was considered as the objective and as the ultimate in DMF reduction with this procedure. In other words, the younger the child when fluoridation started, the better the results.

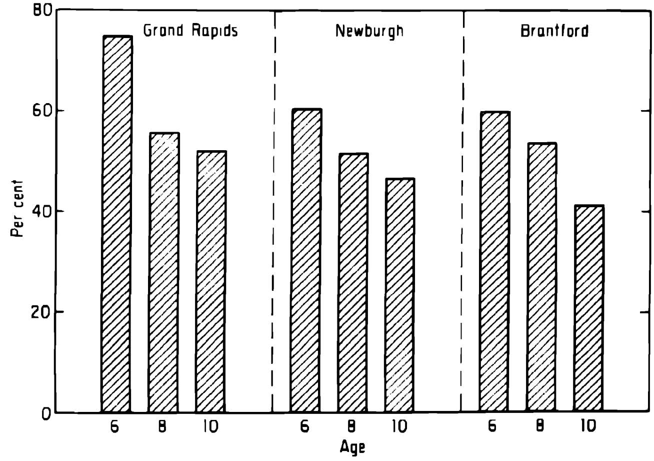

Fig. 3 Reduction in tooth decay at pioneer cities.

TABLE 12-1 Mottled-enamel Experience

City	Fluoride	Number examined	Norm. ques.	Very mild	Mild	Moderate	Moderately severe	Severe	Incidence	Reference
Ankeny, Iowa	8.0	21	0	0	2	10	7	2	100.0	3
Britton, S. Dak	6.6	63	6	11	10	26	- 10 -		90.0	4
Lake Preston, S. Dak	5.9	50	2	5	18	19	- 6 -		96.0	4
Post, Tex	5.7	38	0	0	4	19	13	2	100.0	3
Hecla, S. Dak	5.0	14	1	2	3	8	- 0 -		93.0	4
Pierpont, S. Dak	4.7	26	3	7	9	7	- 0 -		88.0	4
Lubbock, Tex	4.4	176	2	11	54	77	31	1	98.8	2
Conway, S.C	4.0	59	7	12	19	14	7	0	88.2	3
Amarillo, Tex	3.9	168	6	30	58	60	12	2	96.4	2
Platte, S. Dak	3.0	55	19	12	12	10	- 2 -		65.0	4
Plainview, Tex	2.9	78	2	24	24	26	2	0	87.6	2
St. Lawrence, S. Dak	2.9	28	7	6	6	9	- 0 -		75.0	4
Doland, S. Dak	2.9	25	9	2	10	4	- 0 -		64.0	4
Ipswich, S. Dak	2.8	53	20	15	12	5	- 1 -		63.0	4
Redfield, S. Dak	2.7	48	19	14	5	9	- 1 -		60.0	4
Carthage, S. Dak	2.6	34	16	8	8	2	- 0 -		52.0	4
Onida, S. Dak	2.6	31	20	6	5	0	- 0 -		35.0	4
Colorado Springs, Colo	2.5	54	18	14	10	11	1	0	66.6	1
Wolsey, S. Dak	2.4	16	4	2	6	4	- 0 -		75.0	4
Gettysburg, S. Dak	2.4	53	24	16	8	3	- 2 -		55.0	4
Leola, S. Dak	2.3	31	15	10	6	0	- 0 -		51.0	4
Clovis, N. Mex	2.2	138	40	33	49	15	1	0	71.0	3
Miller, S. Dak	2.2	51	26	15	7	3	- 0 -		49.0	4
Iroquois, S. Dak	2.1	28	10	8	5	4	- 1 -		64.0	4

Galesburg, Ill. (first study)	1 9	39	24	11	3	1	0	0	38 5	1
Galesburg, Ill. (second study)	1 9	243	129	82	29	-3-		0	46.9	5
Elmhurst, Ill ..	1 8	170	102	51	15	2	-0-		40 0	6
Monmouth, Ill. (first study)	1 7	29	15	12	2	0	0	0	48 3	1
Monmouth, Ill. (second study)	1 7	99	32	47	20	-0-		0	67 7	5
Aberdeen, S. Dak	1 7	166	129	24	10	3	-0-		22 0	4
Webster City, Iowa	1 6	47	31	13	3	0	0	0	34 0	3
East Moline, Ill	1 5	94	70	18	5	1	0	0	25 5	3
Howard, S. Dak	1 4	48	39	6	3	6	-0-		18 0	4
Joliet, Ill .	1 3	447	334	99	14	0	-0-		25 3	6
Maywood, Ill	1 2	171	114	50	7	0	-0-		33 3	6
Aurora, Ill	1 2	633	538	88	7	0	-0-		15 0	6
Mullins, S.C	0 9	47	42	4	1	0	0	0	10 6	3
Big Spring, Tex	0 7	68	66	2	0	0	0	0	2 9	2
Junction City, Kans	0 7	93	91	2	0	0	0	0	2 1	3
Pueblo, Colo	0 6	49	47	2	0	0	0	0	4 0	1
Elgin, Ill	0 5	403	386	14	3	0	0	0	4 2	6
Macomb, Ill	0 2	63	62	1	0	0	0	0	1 6	5
Quincy, Ill	0 2	291	291	0	0	0	0	0	0 0	5
Lake Michigan—Evanston, Oak Park, Waukegan Ill	0 0–0 1	1,008	1,001	0	0	0	0	0	0 2–1 6	6

"Highest concentration of fluoride incapable of producing a definite degree of mottled enamel in as much as 10% of the group examined."

"Evidence is presented that amounts of fluoride (F) not exceeding one part per million are of no public health significance."

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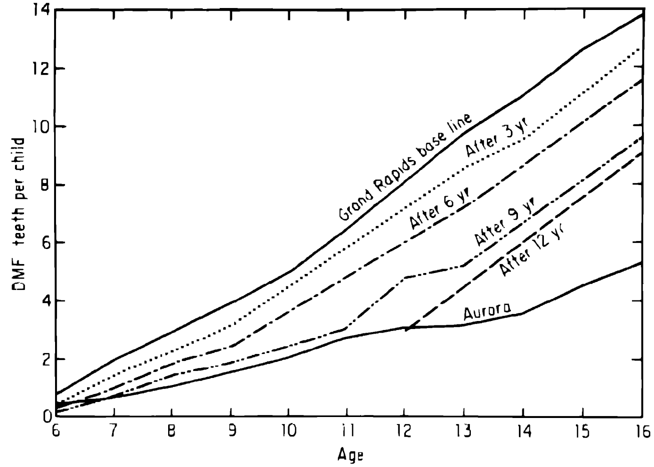


Fig. 4 Comparison of DMF experience in Grand Rapids and Aurora.

4. Children whose permanent teeth were already present in the mouth at the time fluoridation started derived a measurable benefit. For instance, the 16-year-old children who were 6 at the start of fluoridation showed a 26 per cent DMF reduction in 10 years.

Except for the effect on the teeth, no other changes of any sort, adverse or beneficial, have ever been found as a result of fluoridated water in the amounts recommended. This conclusion, of course, had been observed many thousands of times among individuals living in those communities with the natural fluoride content now considered optimum. In order to confirm this, in some of the cities where the fluoride levels were controlled, projects included medical and dental observations of varying complexities in addition to those related to the computation of DMF. These examinations included fluorosis prevalence (mottling of the teeth), x-ray examinations of various joints and parts of the spine, laboratory tests of the blood and urine, and thorough clinical examinations of the children in the groups (as at Newburgh, New York).

Observations which were made in the areas containing water supplies with natural fluorides and which related to fluorosis incidence were confirmed in the fluoridation-study projects where the fluoride levels were controlled. At Grand Rapids, for instance, it was found that approximately 4 per cent of the children 11 years of age had a very mild degree of mottling, whether or not caused by the fluorides in water. This degree of mottling is practically unnoticeable and is of no aesthetic or public health significance; in fact, it has to be searched for quite diligently by dentists who are experienced in making such examinations. In appearance it is a slight, white, opaque flecking of a portion of no more than two or three of the side and rear teeth.

It is this complete absence of any ordinarily noticeable discoloration that provides the best indication of the constant rate of water consumption among children. If several instances of even mild fluorosis in any of the controlled fluoridation studies had occurred, it would have been presumed that such children had consumed an excessive amount of water during the critical period of their tooth enamel formation. Actually, not a single such instance has so far been observed. In other words, even though there is undoubtedly a difference in the amounts of water children drink, the variation is not large enough to produce a noticeable fluorosis from the fluorides contained in their drinking water. This is believed to be one of the most significant justifications for using drinking water as the medium or carrier of the fluoride required for optimum caries reduction. No other suggested media are believed to have the same pattern of constant, relatively unvarying consumption as has been demonstrated for water.

In regard to all other physical examinations and observations in all of the studies so far reported, a typical conclusion is: "No differences of medical significance could be found between the two groups of children."

GROWTH AND PRESENT STATUS

The acceptance of fluoridation in the United States has increased steadily since the first installation at Grand Rapids, Michigan, in 1945. As shown in Fig. 6 the growth has been particularly rapid since 1951, when the beneficial results were first announced. The most rapid growth occurred during

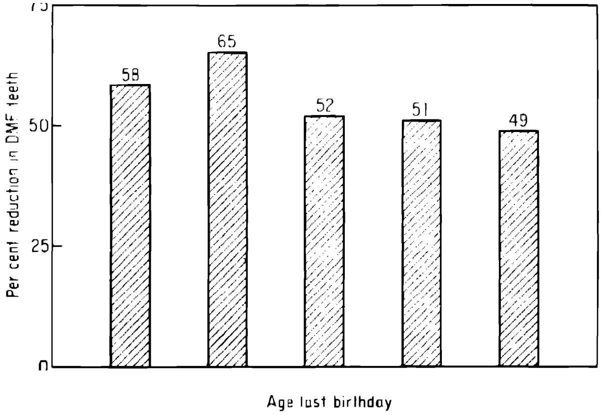


Fig. 5 Reduction in tooth decay in specific age groups 15 years after fluoridation at Grand Rapids, Michigan. (*USPHS.*)

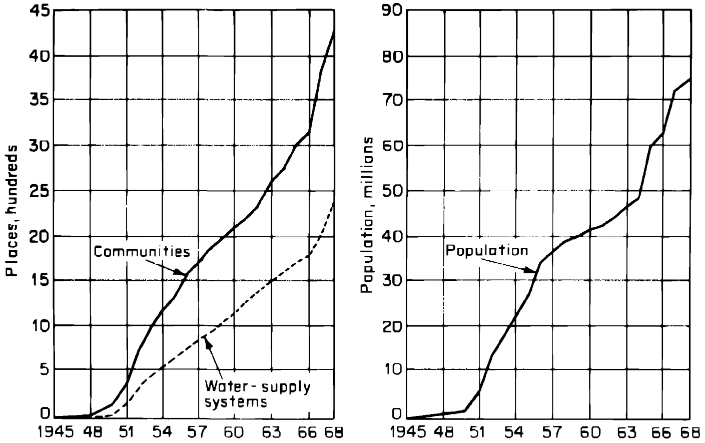


Fig. 6 Communities, water-supply systems, and population served with fluoridated water.

the period from 1950 to 1953 (Table 12-2). It was at this time that active, organized opposition to the measure began, with the result that during the next 10 years a total of 60 water-supply systems elected to discontinue it, although 26 have reinstituted fluoridation after further consideration. At the end of 1969, approximately 2,653 water-supply systems were expected to be furnishing fluoridated water to 4,834 communities where more than 80 million persons lived. In addition, 10.0 million persons were using water naturally containing 0.7 mg/l fluoride or more from public sources. This total of over 90 million persons using fluoridated water in amounts considered effective for caries control represents about 55 per cent of the people in the United States served by public water supplies.

Puerto Rico has the highest proportion (93 per cent) of people receiving this benefit of any country in the world. Approximately 200 cities in 27 countries (outside the United States and Canada) have adopted fluoridation, but so far many of these (except in Latin America) are considered experimental.

A census of places fluoridating, including a list of names of such places in the United States and Canada, is published each year by the American Water Works Association, which has also published a bibliography of fluoridation papers.[1]

An excellent summary of the operating experience, methods, and costs at 20 of the larger cities was completed by New York University during 1957. Of particular interest in the vast array of information:

1. Fluoridation costs averaged $1.23 per million gallons of water treated (7.9 cents per person per year), which includes all items of expense connected with the feeding and control of fluoride compounds.

2. There is no evidence of fluorides accumulating in the mains or of any uncontrollable health hazards among waterworks operators who handle fluoride compounds.
3. All the cities studied were able to maintain the desired fluoride levels for long periods of time, and no instances of prolonged overdosages have been experienced since the projects were started.

DETERMINING OPTIMUM FLUORIDE LEVELS

The optimum fluoride level in water (1.0 ppm in the latitude of Kansas City–Chicago) has been shown to be that level which produces the greatest protection against caries with the least hazard of fluorosis. This figure was obtained after examining the teeth of thousands of children living in places

TABLE 12–2 Annual Cumulative Findings on the Institution of Controlled Fluoridation, Showing Number of Communities, Water-supply Systems, and Population Served, 1945–1968

Year	Fluoridation status at end of each year		
	Number of communities	Number of water-supply systems	Population*
1945	6	3	231,920
1946	12	8	332,467
1947	16	11	458,748
1948	26	13	581,683
1949	49	29	1,062,779
1950	100	62	1,578,578
1951	368	171	5,079,321
1952	751	353	13,875,005
1953	1,007	482	17,666,339
1954	1,194	572	22,336,884
1955	1,347	672	26,278,820
1956	1,583	772	33,905,474
1957	1,717	879	36,215,208
1958	1,890	995	38,461,589
1959	1,990	1,081	39,628,377
1960	2,111	1,172	41,169,412
1961	2,197	1,249	42,201,115
1962	2,321	1,350	44,045,392
1963	2,612	1,482	46,678,380
1964	2,758	1,573	48,363,066
1965	3,030	1,692	59,855,024
1966	3,145	1,785	62,427,290
1967	3,827	2,091	71,916,682
1968	4,229	2,372	74,579,666
1969	4,834	2,653	80,096,860

*Includes adjustment for population growth during intercensal years 1951–1959 based on results of the 1960 census of population.

with various fluoride levels in the water. It was not based on any direct or accurate knowledge of how much water children drank at various times and at different places. Early in such investigations, it was observed that this optimum figure varied, depending on the local air temperature, which had a direct bearing on the amount of water children at different ages consumed.

Studies in California and Arizona, where temperatures are considerably above the average of other parts of the United States, showed a definitely lower optimum fluoride level. This was demonstrated by observing dental fluorosis prevalence in places with various natural fluoride levels in their public water supplies and by estimating the actual quantities of water ingested by children of various age groups and weights. In areas where the mean annual temperatures are greater than 70 °F, the optimum fluoride concentration should not exceed 0.8 ppm. This relationship, compared with Dr. Dean's data from areas with mean annual temperatures of 50 °F, is shown in Fig. 7. Later a formula was derived for determining fluoride levels at any temperature:

$$\text{ppm fluoride} = 0.34/E \qquad (1)$$

where E is the estimated average daily water consumption for children through 10 years of age in terms of ounces of water per pound of body weight. E is obtained from the formula:

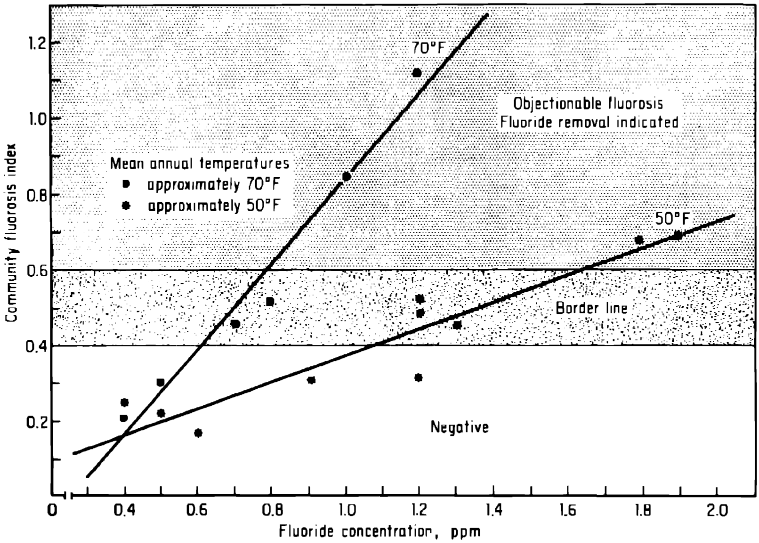


Fig. 7 Relationship between fluoride levels, fluorosis, and temperature. (*USPHS*.)

$$E = 0.038 + 0.0062 \times \text{average maximum temperature, } ^\circ\text{F} \qquad (2)$$

Table 12-3 shows the fluoride levels obtained using this formula when various local temperature averages are applied.

TABLE 12-3 Mean Maximum Temperatures and Corresponding Recommended Optimum Fluoride Concentrations

Mean maximum temperatures	Recommended optimum fluoride concentration
50.0–53.7	1.2
53.8–58.3	1.1
58.4–63.8	1.0
63.9–70.6	0.9
70.7–79.2	0.8
79.3–90.5	0.7

A large number of water supplies contain fluorides naturally. Table 12-4 shows the distribution of these based on the number of communities served by supplies with various fluoride levels. This table shows that approximately 500 supplies should be either defluoridated or diluted to the point where the fluoride level is maintained at the optimum. The large number of supplies containing some, but not enough, fluorides raises the question of the practicability of supplementing the natural fluorides with enough fluoride to bring the concentration up to the optimum level. Usually, it can be shown that even though very little more fluoride is needed, it is economically justifiable to add it.

TABLE 12-4 Communities Grouped According to Fluoride Concentrations Occurring Naturally

Fluoride content	Number of communities	Population
0.0–0.6	17,963*	148,627,765
0.7–1.2	1,517	5,782,628
1.3–2.0	589	1,366,533
2.1–3.9	386	712,253
4.0 and over	138	245,021
Total	20,593	156,734,300

*Includes 4,229 communities adding fluorides in controlled amounts.

In Fig. 8, which is based on DMF results of 57 studies in various cities, an increase in fluoride level from 0.5 to 1.0 ppm produces a decrease of approximately two DMF teeth per person; and an increase of from 0.7 ppm to 1.0 ppm produces a decrease of about one DMF tooth per person.

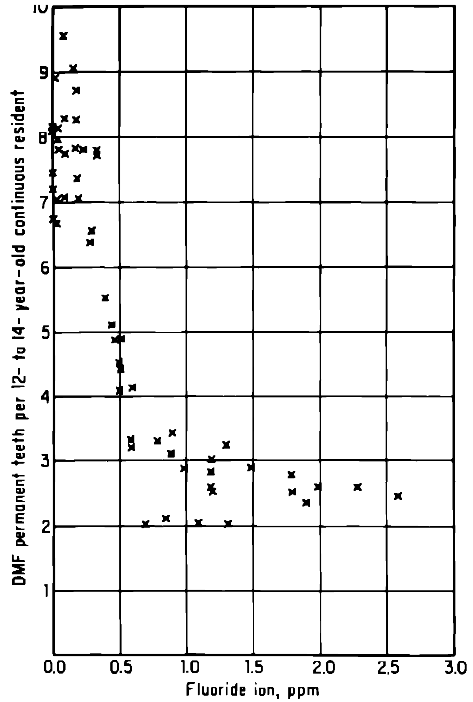


Fig. 8 Relationship between fluoride levels and prevalence of dental decay.

MAINTAINING FLUORIDE LEVELS

Fluorides must be fed accurately in water treatment. From the point of view of optimum reduction in dental decay, a difference of only 0.3 ppm fluoride below the optimum level will, on the average, produce about one additional decayed tooth in 13-year-old children. On the other hand, prolonged use of water containing fluorides in excess of the optimum will produce some mottling (dental fluorosis). After the optimum level is determined, deviations greater than 0.1 ppm (10 per cent when optimum level is other than 1.0 ppm) should not be tolerated. A considerable amount of evidence is available to show that when prolonged deviations occur, the effect on children's dental health is apparent. For instance, when the fluoride concentrations have been maintained at variable and consistently lower levels than the optimum, the DMF rates have been much higher than in similar communities where the level has been maintained correctly.

Frequent determination of the fluoride content of water samples is one of the two ways available to prove the adequacy of fluoridation. The results of such laboratory testing for fluorides reveal the concentration at the instant the sample was collected. Similar results, useful in furnishing a check on the laboratory results, are obtained by computing the fluoride dose for each day. This computation is based on the quantity of fluoride compound used and the amount of water treated. A sample of water taken at any time during the day should, when analyzed, contain within 0.1 ppm of the fluoride concentration found by this computation. Samples should be analyzed at least once a day in the smallest plants, more often in the larger ones. The methods of analyses described in *Standard Methods for the Examination of Water and Wastewater* should be used for the fluoride determinations. Among the factors which affect the accuracy of fluoride analysis are:

1. *Interferences.* If the presence of interfering ions is known or suspected, the sample should be distilled prior to colorimetric analysis. This is particularly true of raw water samples. The amount of fluoride in the raw water will affect the amount of fluoride to be added.
2. *Sampling point.* This should be chosen with care, since subsequent treatment processes may lower the fluoride level, prior treatment processes may introduce interfering ions, or the site chosen could result in a nonrepresentative sample if it is at a point where, for instance, insufficient mixing has taken place.
3. *Analytical procedure.* The fluoride test is extremely sensitive and can be affected by such things as cleanliness of glassware, accuracy of measurement of sample and reagent, temperature, matching of Nessler tubes (in the visual method), timing of color development (in the alizarin methods), and preparation of the reagents and standards.
4. *Color, turbidity, and chlorine.* These must be considered as interferences. Chlorine may be removed by arsenite, but color and turbidity usually require distillation for removal.
5. *Sample dilution.* The range of the fluoride reagents is limited, and occasionally samples are encountered which require dilution prior to analysis. It should be remembered that the sample must be diluted prior to the addition of reagent and that the volume of diluted sample taken for analysis be equal to the volume of sample required by the procedure. Results obtained from a diluted sample must be multiplied by the correct dilution factor. This is also true of samples resulting from steam distillation, which produces a diluted sample.
6. *Age of reagents.* The life of the zirconium-alizarin reagents is somewhat limited, and old reagents produce colors too pale to use in the visual method and lose sensitivity in the photometric method.

Permanent color standard kits are available for fluoride determination, and while they do not possess the inherent sensitivity of the *Standard Methods,* the above precautions still apply. In addition, the directions furnished by the kit manufacturer must be followed explicitly. Two publications in the *Journal of the American Water Works Association* describe the limitation of kits for fluoride analysis.[2] [3]

FLUORIDE COMPOUNDS IN USE

The most abundant minerals containing fluorides are fluorspar (which contains calcium fluoride); cryolite (in which the fluorides are combined with aluminum and sodium); and apatite (which is usually a calcium compound of phosphates, fluorides, carbonates, and sulfates). Fluorine as a chemical element (not combined with any other element to form a chemical compound) does not exist free in nature. Elemental fluorine is now being manufactured and is available in large quantities as a gas, but its cost and the extreme hazards associated with its handling will make it unsuitable as a water fluoridating agent.

Fluoride compounds are estimated to constitute about 0.08 per cent of the earth's crust (with seawater usually containing about 1.0 ppm fluorides); and as such, fluorine ranks about thirteenth among the elements in order of abundance. The fluorides found naturally in water are probably derived principally from the three minerals mentioned above. Fluorides are found in almost all water supplies; some sources contain too much, most contain too little, while a few have just the right amount for optimum dental health.

There follows a description of the several fluoride compounds presently used by water systems. Additional information about them is available in Chapter 17, "Chemicals and Chemical Handling."

Fluorspar is the principal raw material for the commercial fluoride compounds available at the present time even though known deposits of phosphate rocks (apatites) may contain more fluorides. Technical and economic problems still remain to be overcome if fluorides (other than the silicofluorides) obtained from apatites are to compete successfully with those formed from fluorspar. Cryolites have a higher fluoride content, but deposits are relatively small.

Fluorspar is a mineral containing varying amounts of calcium fluoride (CaF_2). Pure calcium fluoride contains 51.1 per cent calcium and 48.9 per cent fluoride. Commercial grades of fluorspar usually contain from 85 to over 98 per cent calcium fluoride.

Normal consumption of fluorspar in this country has averaged over 500,000 tons per year since World War II. In 1963, for example, 200,000 tons were produced in domestic mills, and over 550,000 tons were imported, with almost three-quarters of this amount coming from Mexico.

Removal of the impurities from the fluorspar ore is accomplished by grinding, flotation of the slurry, filtration, and drying.

For the fluoridation of water, fluorspar is used in two ways: the mineral can be dissolved in an alum solution at the water plant and fed as a liquid into the water; or, it can provide the principal raw material in the manufacture of various fluoride-containing compounds which are commercially available and which can be fed either as a liquid or as a solid directly into

TABLE 12-5 Characteristics of Fluoride Compounds

Type	Calcium fluoride (CaF_2)	Sodium silicofluoride (Na_2SiF_6)	Sodium fluoride (NaF)	Hydrofluosilicic acid (H_2SiF_6)	Magnesium silicofluoride ($MgSiF_6{\cdot}6H_2O$)	Ammonium silicofluoride ($(NH_4)_2SiF_6$)	Potassium fluoride ($KF{\cdot}2H_2O$)
Form	Powder	Powder	Powder or crystal	Liquid	Crystal	Crystal	Crystal
Molecular weight	78.08	188.05	42.00	144.08	274.48	178.14	94.13
Commercial purity, %	85–98	98.5	90–98	22–30	98	98	98
Fluoride ion, % (100% pure material)	48.8	60.7	45.25	79.2	41.5	63.9	20.2
Weight, lb/cu ft	101	55–72	65–90	10.5 lb/gal	73	81	58
Storage space, cu ft/1,000 lb fluoride ion	21–24	23–30	22–34	54–73	34	21	87
Lb Reqd/mg for 1.0 ppm fluoride at indicated purity	17.6(97%)	14.0	18.8(98%)	35.2(30%)	20.5	13.3	42.1
Solubility, g/100g H_2O at 25°C (77°F)	0.0016	0.762	4.05	Infinite	64.8(17.5°C)	18.5(17.5°C)	100
Gal sat. sol. reqd/mg water at 25°C and 1.0 ppm fluoride	132,000	219	55.6(98%)	3.35	3.5	8.0	8.0
pH of saturated solution	6.7	3.5	7.6	1.2(1% sol.)	1.0	3.5	7.0
Cost as of 1967							
¢ per lb	2.2	7.25	14.4	7.0(30%)	13.0	15.0	37.5
¢ per lb available fluoride	4.8	12.0	32.5	29.5	32.0	23.9	189.0
Per mg for 1.0 ppm	$.40	$1.00	$2.72	$2.46	$2.66	$2.00	$15.77
Per year at 1.0 mgp	$146.00	$365.00	$990.00	$900.00	$973.00	$730.00	$5,760.00

the water to be treated. The primary compound manufactured from fluorspar is hydrofluoric acid, from which is produced most fluoride-containing salts, including sodium fluoride. This acid, as such, is never used in water fluoridation because of the dangers involved in handling it.

Dissolving the fluorspar at the water plant is by far the most economical of all fluoridation processes. The cost in 1964 of a pound of fluoride ion derived from the more commonly used and commercially available fluoride compounds is given below:

Compound	*Cost, cents per lb available fluoride ion*
Calcium fluoride	4.8
Sodium silicofluoride	13.5
Ammonium silicofluoride	24.0
Hydrofluosilicic acid	40.0
Magnesium silicofluoride	32.0
Sodium fluoride	32.5

It is for this economic reason that fluorspar might be used whenever other factors in a water plant permit the use of this inexpensive material.

The process of using fluorspar involves a means for dissolving calcium fluoride, which is almost insoluble in water. It has long been known that calcium fluoride is soluble in strong acids or in solutions of aluminum compounds. If strong acids are used, the resulting mixture would be more expensive to prepare than many of the other compounds used for fluoridation. The use of solutions containing aluminum compounds is considerably more practical in that one of the more commonly used chemicals routinely employed in water plants as a coagulant of impurities is filter alum (aluminum sulfate).

As a result of this chemical phenomenon, it was found that by varying the concentration of alum in solution, any desired quantity of fluoride could be obtained from fluorspar. A saturated solution of calcium fluoride contains (as fluoride) about one-tenth of the alum concentration. For example, a 10% alum solution would produce a saturated fluoride solution containing 1.0 per cent fluoride. Any fluoride solution strength can therefore be obtained by changing the strength of the alum solution.

Fluorspar is dissolved in an appropriately designed tank equipped with a mixer and overflow weir. Such tanks have been built and are now successfully being operated at the water-treatment plants serving Bel Air, Maryland, and Rosiclare, Illinois. The installation at Bel Air was begun in July, 1956. The tanks are intended to hold an excess of fluorspar in contact with the alum solution for a designated period of time; to provide an area of intense agitation; to separate, hydraulically, the fluorspar from the small amount of gypsum formed when the fluorspar dissolves; and to remove the mixed alum-fluoride solution and the gypsum.

A constant rate of alum solution addition is provided in order to suspend the gypsum and to remove it from the tank. The fluoride dose is changed by varying the alum solution concentration in the dissolving tank (this is done by changing the alum-water ratio in the alum-feeder dissolving chamber or by making up the solution to correct strength in batches). The alum dose is changed by varying the setting on the alum feeder. In order to maintain the same alum concentration after this change, the water rate into the chamber must be changed. With these combinations any alum dose with any accompanying fluoride level can be introduced into the water within the range of the fluorspar dissolver designed for a particular water-treatment plant.

The cost of fluorspar dissolvers varies widely, depending on their size and the variety of appurtenances. These costs can be written off in a very short time because of the marked savings realized through the use of the less expensive fluorspar.

The cost of fluorspar varies according to the quality. Almost any quality can be used in this process, but local conditions may indicate that one grade is more desirable. There are three commercially available grades: metallurgical, ceramic, and acid. Purity ranges between 72½ and 97 per cent.

The various grades weigh, on the average, about 100 lb/cu ft and as such require about 22 cu ft of storage space per 1,000 lb of fluoride ion. Fluorspar can be shipped in bulk or, for the smallest plants, in 100-lb paper bags.

Sodium Fluoride

After the acidulation of fluorspar with sulfuric acid, the hydrofluoric acid formed can be used as the starting compound for many fluoride-containing salts.

Sodium fluoride is the only compound used at present for the fluoridation of municipal water supplies which is manufactured from hydrofluoric acid. Sodium carbonate is used to neutralize hydrofluoric acid when making sodium fluoride.

Sodium fluoride is a white, odorless, free-flowing material available either as a powder or as a mixture of various-sized crystals. Its formula weight is 42.00, its specific gravity is 2.79, and its solubility is practically constant at 4.0 grams per 100 ml of water at temperatures generally encountered in water-treatment practice. The pH of saturated solutions varies with the source (method of manufacture) and type of impurities. Generally, at present, sodium fluoride solutions have a pH close to neutrality. Purities range between 90 and 98 per cent. The impurities consist of water, free acid (or alkali), sodium silicofluoride, sulfites, and iron. The specifications included in the *American Water Works Association Standards* (AWWA B701-60) suggest that the following impurities should not exceed the respective limits (per cent):

Insoluble matter	0.50
Moisture	0.15
Fluosilicate	0.35
Heavy metals (as lead)	0.01
Iron (as Fe_2O_3)	0.07
Other	3.92

The density of sodium fluroide can vary from a light grade (less than 65 lb per cu ft) to heavy (90 lb per cu ft), depending on the method of manufacture. A material weighing 65 lb per cubic foot has a sieve analysis of 99 per cent through 200 mesh and 97 per cent through 325 mesh. A crystalline grade which contains practically no particles capable of forming dust and which is ideally suited for the automatic production of a saturated (4.0 %) solution has a mesh size of approximately 100 per cent through 20 mesh and only 2 per cent through 60 mesh. Some state regulations require that sodium fluoride and other fluoride compounds be tinted a blue color in order to distinguish them from other water-treatment chemicals. Tinting raises the cost of the material about 1 cent per lb.

During 1962, over 5½ million people using 452 water-supply systems used water fluoridated with sodium fluoride. Bulk shipments are permitted under the Consolidated Freight Classification issued during January, 1963. Depending on purity and density, this compound requires between 22 and 24 cu ft per 1,000 lb of fluoride ion.

Silicofluorides

Most of the commercially available silicofluorides are obtained as byproducts of the purification of phosphate rock. The primary products are superphosphates, phosphoric acid, elemental phosphorous, and triple superphosphate. Most of these products are used in the preparation of chemical fertilizers.

The most important deposits of phosphate rock are in the United States, with extensive reserves in Florida, Tennessee, and some of the Western states. Other large deposits are in North Africa, the U.S.S.R., and various islands in the Indian and Pacific Oceans. In the United States the known domestic reserves in 1950 amounted to more than 13 billion tons, which contained 420 million tons of fluorine. The fluorine from this source alone would be sufficient to supply all that would be required to fluoridate all the public water supplies in the United States for the next 27,000 years or so. During the production of phosphates in 1956, 460,000 tons of fluorine were made available. Only 15,000 tons of fluorine per year are required to fluoridate all the public water supplies in the United States.

After the phosphate rock is ground, it is treated with sulfuric acid, which not only dissolves the calcium phosphate but when combined with the fluorine and silica forms silicon tetrafluoride. This gas is reacted with water, from which is obtained hydrofluosilicic acid. A large portion of the silicon tetrafluoride formerly escaped without combining with the water and was discharged from the plant with the stack gases. This created a considerable nuisance in the neighborhood and a hazard to the employees. It is customary now to absorb the gas in water or in beds of limestone to form calcium fluoride. At present only a minor portion of the fluorides are converted to the acid—about 29 per cent of the Florida phosphate rock—and the remainder is left in the superphosphate. Of this 29 per cent, only about one-sixth is recovered for fluosilicic acid production, the rest being diluted and discharged as waste. The very low rate of recovery is predominately due to the lack of economic incentive for producing silicofluorides and to the ease with which they can be disposed of at present. A larger proportion will probably be recovered in the future because of the increased awareness of the deleterious effects of stream and air pollution.

Hydrofluosilicic Acid

Hydrofluosilicic acid (fluosilicic acid, hexafluosilicic acid, silicofluoric acid) is a 20 to 35% aqueous solution of H_2SiF_6 with a formula weight of 144.08. The anhydrous form of the acid (containing no water) is not known. It is a colorless, transparent, fuming, corrosive liquid having a pungent odor and an irritating action on the skin. A 22% solution boils at about 221 °F and freezes at about 4 °F. A 1.0% solution has a pH of 1.2. The density of the 22% acid is 1.194.

In manufacturing this acid, the silicon tetrafluoride is drawn by fans through a tower equipped with trays. Here the gases are absorbed in recirculated fluosilicic acid. When the acid reaches the desired strength, the system is discharged to filters where some of the free silica is removed. The maximum concentration attained by this method is 30%.

While this acid is only slightly volatile, care should be observed in avoiding the vapor. Inhalation can cause irritation of the respiratory tract. The acid is relatively safe to handle when compared with hydrofluoric or sulfuric acids. Nevertheless, as soon as possible after exposure, it should be washed off the hands or other parts of the body with liberal amounts of water. Protective clothing and goggles should be worn while handling it.

Upon vaporizing, the acid decomposes to hydrofluoric acid and silicon tetrafluoride. This equilibrium exists at the surface of strong solutions of the acid, and the small concentration of hydrofluoric acid may slowly attack the glass or ceramic container above the solution level. Rubber-lined or plastic containers are generally used for shipping and storage. Storage tanks should be covered and, if placed indoors, ventilated. Storage at lower temperatures reduces volatility. Because of its corrosiveness, care should be taken in selecting materials which will withstand deterioration. Materials best suited for this purpose include: Hastelloy, structural carbon, Durimet 20, neoprene, natural rubber, Saran, Teflon, polyethylene, and Kel-F.

The *American Water Works Association Standard Specifications for Fluosilicic Acid* (AWWA B703-60) limits the total impurities as heavy metals (leads, arsenic, antimony, tin, mercury, and the like) to 0.02 per cent. No limit is placed on silica, although this element is sometimes present in appreciable quantities. When an excess of free silica occurs, a visible, insoluble precipitate forms when the acid is diluted to less than a 20:1 ratio. The precipitate can be avoided by adding hydrofluoric acid to the fluosilicic acid in the ratio of about 1:50. In general, it is not advisable to dilute the acid with water, since this indicates that the water plant involved is using very small amounts of fluoride with a resulting higher cost of the acid compared with the fluoride from other compounds.

Hydrofluosilicic acid is priced on the basis of 30% strength even though the weaker solution may be (and generally is) shipped. This is as expensive as any other compound now being used. Despite this fact, it is being used by more people (over 11½ million in 1962) for water fluoridation than any other compound, with the exception of sodium silicofluoride. This is primarily because three of the largest cities in the United States (Chicago, Baltimore, and Philadelphia) are using it. Each is able to obtain the acid at a very favorable price from local producers.

This acid is shipped in 125-lb rubber-lined drums or in 160-lb or 500-lb lined wooden barrels or steel drums. A reasonably large deposit is required on 500-lb drums. Some manufacturers also have available rubber-lined tank cars and trucks of capacities up to about 90,000 lb net.

Sodium Silicofluoride

Hydrofluosilicic acid is the basic raw material used in the manufacture of silicofluoride salts. There are many of these made, but so far only sodium silicofluoride, magnesium silicofluoride, and ammonium silicofluoride have been used for water fluoridation.

Of all the compounds used for fluoridation, sodium silicofluoride is by far the most popular. It is used to supply more people with fluoridated water (over 25 million during 1962) than all the other compounds combined. The primary reason for this is its low cost. Next to fluorspar, it is the cheapest source of fluoride. While it is difficult to dissolve, this drawback can be overcome by selecting the correct dissolving apparatus. There are some installations feeding slurries (solutions of a compound of such excessive strengths that not all of it can dissolve) of sodium silicofluoride in order to save money on dissolving equipment. This procedure is not ordinarily recommended since undissolved particles of the compound may be fed into the distribution system or may sink to the bottom of a storage tank and be lost. Sodium silicofluoride (Na_2SiF_6) is a white, free-flowing, odorless, crystalline powder. Its molecular weight is 188.05, its density is 2.679, and the pH of a saturated solution is 3.4 to 4.0. The solubility varies between 0.37 and 32°F to about 2.5 grams per 100 ml of water at boiling.

Two grades of fineness are commercially available—regular (72 lb per cu ft) and fluffy (55 lb per cu ft). A typical sieve analysis of the regular grade is 100 per cent through 40 mesh and 95 per cent through 100 mesh; for the fluffy grade, 99.5 per cent through 200 mesh and 97.5 per cent through 325 mesh. The present *American Water Works Association Standard* (AWWA B702-60) limits the heavy metal content to 0.050 per cent and the moisture to 0.05 per cent; insoluble matter to 0.5 per cent commercial purity is generally in excess of 98 per cent.

Solutions of sodium silicofluoride are corrosive, and the materials for piping, valves, pumps, and fittings should be chosen with this in mind. The materials listed for handling hydrofluosilicic acid are also suitable for solutions of this compound.

Paper bags (100 lb net), paper-lined barrels (425 lb net), and fiber drums (125 lb net) are used for shipping sodium silicofluoride. Bulk shipments are permitted under the Consolidated Freight Regulations. The storage space required is equivalent to 23 to 30 cu ft per 1,000 lb of fluoride ion, depending on the density of the material (regular or fluffy).

Ammonium Silicofluoride

This compound is produced by neutralizing fluosilicic acid with either aqueous ammonia or ammonia in the gaseous form. The product of this reaction is centrifuged to remove most of the water and then oven dried. It is sold as a white, free-flowing crystalline material containing few particles capable of producing a dust. A typical mesh size would be 100 per cent through 20 mesh and only 10 per cent through 100 mesh.

Ammonium silicofluoride [$(NH_4)_2SiF_6$] has a formula weight of 178.14, and the 98 per cent pure material contains 72.7 per cent fluorine, 15.4 per cent silica, and 18.75 per cent ammonia. Its solubility is high—up to 55.5 per cent at 212°F—but falls to 13 per cent at 32°F. Its apparent specific gravity is 2.1, and the pH of a saturated solution is 3.5. Its present cost of about 15 cents per lb (23 cents per lb of fluoride ion) makes it economically comparable to sodium fluoride.

The use of this material is particularly desirable at those places where ammonia is used to form chloramines with the chlorine added to the water for disinfection purposes. The use of ammonium silicofluoride provides part or all of the ammonium required for producing chloramine. Theoretically, to form chloramines, the chlorine required is four times the amount of ammonia fed. Inasmuch as 13.3 lb of ammonium silicofluoride is used to produce 1.0 ppm fluoride in a million gallons of water, then 2.5 lb of ammonia would be supplied. There would then have to be fed at least 10 lb of chlorine per million gallons of water to form chloramines. A free residual chlorine would then be produced by any amount of chlorine in excess of 10 lb per million gallons. Ammonium silicofluoride is also used for mothproofing textiles, in the sand-mold casting of magnesium, and as a laundry sour. At present it is used for fluoridation of water supplies in only five communities, serving a total of 66,000 people.

The material is available in 100-lb and 400-lb drums and in carload and truckload lots.

This review of the chemical and physical characteristics of various fluoride compounds is intended to assist prospective users in selecting the one best material for a particular installation. The cost, availability, and quality will vary from place to place so that the final choice must be based on a more or less detailed study of the advantages and disadvantages of each compound. The various characteristics that are ordinarily considered include:

Chemical Costs. Based on the cost of the available fluoride ion, fluorspar is by far the least expensive source. It is believed that whenever aluminum coagulants are used for water treatment, fluorspar should be seriously considered for fluoridation. When fluorspar cannot be used, then sodium silicofluoride should be considered next. After these in order of cost would be placed ammonium silicofluoride, hydrofluosilicic acid, and sodium fluoride.

Solubility. If a gallon of hydrofluosilicic acid is required to fluoridate a certain quantity of water, then 17 gal of a saturated solution of sodium fluoride or 65 gal of a saturated solution of sodium silicofluoride will be required for the same amount of water. The inherent advantage of the acid is reflected in the lower cost of solution feeders and solution tanks as compared with the cost of dry feeders for the solid fluoride compounds. However, this advantage may be lost in the larger installations where the other, less expensive compounds are proportioned with dry feeders.

Chemical Storage Space. For the same quantity of fluoride ion, sodium silicofluoride requires the least storage space, hydrofluosilicic acid the most. However, the acid is stored in tanks which might be placed outdoors or underground. Practically speaking, consideration of storage requirements as a factor in choosing a compound depends on a comparison between costs for providing additional storage space and the local price of the compounds.

Feeder Space Requirements. Hydrofluosilicic acid has been chosen in some communities where available space in small treatment plants is limited. Inasmuch as the acid can be stored in tanks at some distance from the feeder, and no solution makeup equipment is required, the use of the acid is advantageous when room for only the solution feeder is available.

Corrosiveness. Although the relative corrosiveness of fluoride compounds differ, equipment manufacturers provide about the same corrosion-resisting materials for solution feeders, tanks, and appurtenances regardless of the compound used. About the only exception is the action of hydrofluosilicic acid on ceramic crocks or glass-lined tanks (as a result of vaporization and the formation of small amounts of hydrofluoric acid on the liquid surface). However, hydrofluosilicic acid will seldom be used in such containers because it can be withdrawn directly from the rubber-lined drums in which it is shipped or stored.

Incrustation in Feeding Equipment. Incrustants form occasionally in solution tanks, feeders, and feeder lines. These are essentially calcium and magnesium fluoride or silicofluoride derived from strong fluoride solutions and the hardness constituents of the water. No incrustants are formed when hydrofluosilicic acid is used because it is not ordinarily diluted with water. The incrustants formed when sodium silicofluoride is used are slightly more soluble than calcium or magnesium fluoride (formed with sodium fluoride). The problem can be minimized by softening the solution water or applying small amounts of hexametaphosphates.

There is very little additional labor involved in removing the precipitated fluorides from solution or saturator tanks, inasmuch as sodium fluoride contains an amount of insoluble material which also must be removed periodically.

Bulk Chemical Handling. Relatively little manual labor is required in treatment plants where hydrofluosilicic acid is used because this material can be pumped. In the larger plants, where carload shipments in bulk are feasible, the dry powdered or crystalline materials can be easily and economically handled with mechanical or pneumatic conveyors. Considerable effort is required in the medium-sized plants receiving their chemical in barrels or bags. They must be moved about the plant and emptied by hand into the feeder hoppers or solution tanks. In general, hydrofluosilicic acid requires the least handling in any plant, while the effort required in handling the dry material depends on the size of the plant.

Hazards to Operators. Dust arising from the transfer of powdered fluorides can be controlled by careful handling; by the use of protective devices (masks, dust collectors, gloves, goggles, and the like); and by specifying particle sizes which produce little dust. Practically no hazards are involved in using the acid because it is ordinarily proportioned directly from the shipping containers. At some of the smaller plants where the acid requires dilution, considerably more care is required for safe handling. No particular advantage is gained by this procedure, however, because about as much effort is required to dilute the acid as to make up solutions of the less expensive dry materials.

METHODS OF FEEDING FLUORIDES

Devices for feeding fluorides have generally been adapted from those machines originally designed for accurately feeding a large variety of liquid and solid chemicals in the industrial and water-treatment fields.

Fluorides are proportioned into a water supply either as liquids or solids. Chemical feeders can therefore be broadly divided into two types: (1) solution feeders, which are essentially small pumps used to feed a carefully measured quantity of accurately prepared fluoride solution (or hydrofluosilicic acid) during a specified time; and (2) dry feeders, which deliver a predetermined quantity of the solid material during a given time interval. Dry feeders are further subdivided by types, depending on the method of controlling the rate of delivery. Volumetric dry feeders deliver a measured volume of dry chemical within a given time interval; gravimetric (loss-in-weight) feeders deliver a measured weight of chemical within a given period.

The choice of a feeder depends on the fluoride compound used and the amount to be fed. The rate of feed will depend on the desired fluoride content of the treated water, the amount of water to be treated passing a given point, and the fluoride content of the untreated water. In general, solution feeders are used for the smaller supplies and dry feeders for the larger ones. There is, of course, a wide area within which either type would be equally successful. The capacities of the various feeders for introducing 1.0 ppm fluoride into water at different rates of flow are shown in Table 12-6.

SOLUTION FEEDERS

Solutions of fluorides can be fed into a water supply in the following ways:

1. Saturated solutions of sodium fluoride in constant strengths of practically 4 per cent can be produced in a saturator tank at almost any temperature of water encountered in the usual water plant. A diagram of this device is shown in Fig. 9. The tank is made of stainless steel or fiberglass and is equipped with an inner cone connected to a tube through which the suction line from the feeder passes. The cone is covered with a bed of graded sand and gravel on which the crystalline sodium fluoride rests. Up to about 200 lb sodium fluoride is added to the tank together with the water. A float valve automatically maintains a constant water level over the sodium fluoride bed. The water slowly trickles down through the sodium fluoride and becomes saturated with it before it reaches the sand and gravel. It is then withdrawn from the saturator with a solution feeder. Figure 9 also shows two tanks which, as explained later, are sometimes included to soften the water.

TABLE 12–6 Usual Range of Fluoride Feeders

Type of feeder	Chemical used	Feed-rate range		Gpm treated with 1.0 ppm F	
		Minimum	Maximum	Minimum	Maximum
Gravimetric dry feeder	Na_2SiF_6	0.5 lb per hr	5,000 lb per hr	600	6,000,000
	NaF	0.5 lb per hr	5,000 lb per hr	440	4,400,000
Volumetric dry feeder	Na_2SiF_6	1.0 oz per hr	5,000 lb per hr	75	6,000,000
	NaF	1.0 oz per hr	5,000 lb per hr	55	4,400,000
Piston or centrifugal pump	Solution of 22% H_2SiF_6	0.375 ml per min	Unlimited	18	Unlimited
	Solution of 4% NaF	0.375 ml per min	Unlimited	2	Unlimited
Diaphragm pump	Solution of 22% H_2SiF_6	2.0 ml per min	1 gpm	110	210,000
	Solution of 10% $(NH_4)_2SiF_6$	2.0 ml per min	1 gpm	34	65,000
	Solution of 4% NaF	2.0 ml per min	1 gpm	9.5	18,000

Some small amount of insoluble material will always collect on top of the bed, and arrangements must be made to remove it periodically, usually about once a year. This can be most readily done by introducing water under pressure down the tube containing the feeder suction hose. The insoluble particles resting on top of the bed will generally rise with the water introduced through the gravel and can be removed through the overflow pipe near the rim of the tank.

2. Unsaturated solutions of sodium silicofluoride, sodium fluoride, magnesium silicofluoride, or ammonium silicofluoride are prepared by weighing amounts of the compounds, measuring quantities of water, and thoroughly mixing them together. Errors are therefore possible in weighing the compound, in measuring the quantity of water, and in mixing insufficiently. Any one of these errors will result in a solution different from the strength intended and consequent variations in the fluoride content of the treated water.

3. Solutions of hydrofluosilicic acid are used either as delivered (22 to 30 per cent) or, if necessary, diluted with water to definite strength. Again, as in method (2), attempts to dilute the acid are subject to errors in measuring both the acid and the diluting water. It is much better to use the acid undiluted as it comes from the containers in which it is shipped. If the acid is too concentrated for the solution feeder to handle, then weaker solutions of other, less expensive compounds are generally indicated, e.g., saturated solutions of sodium fluoride. If the acid must be diluted, care

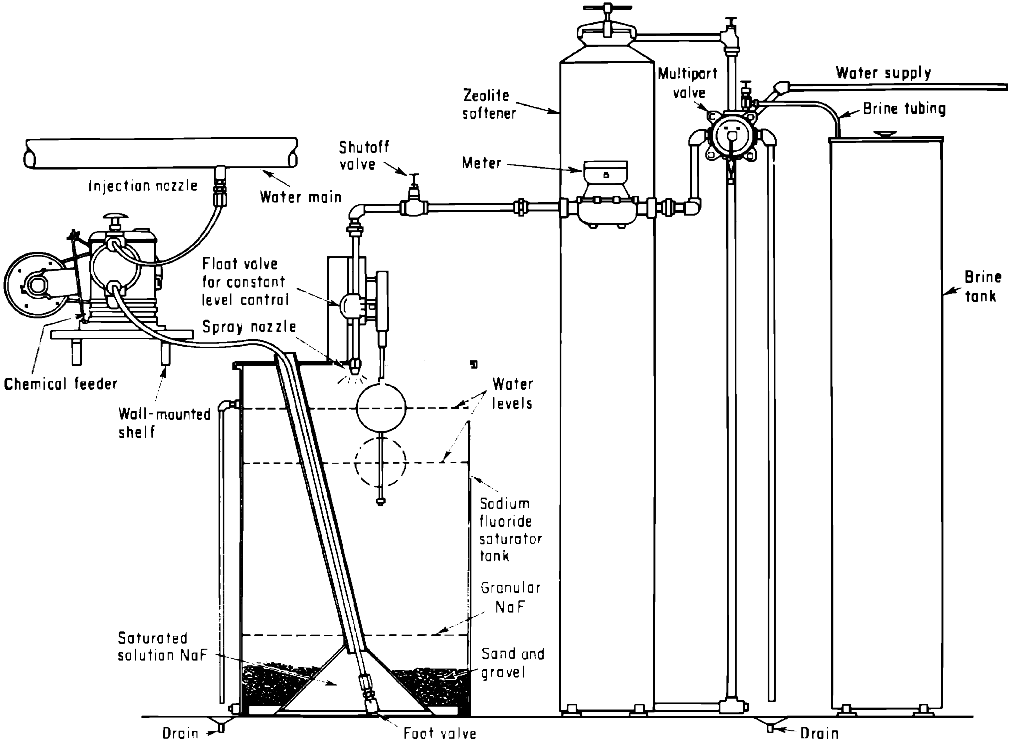


Fig. 9 Sodium fluoride saturator. (*B-I-F Industries, Inc.*)

should be taken to avoid the formation of a precipitate of silica which will appear despite the quality (hardness) of the water used for dilution. This can invariably be avoided by specifying that the acid should be fortified with hydrofluoric acid so as to dissolve all the uncombined silica.

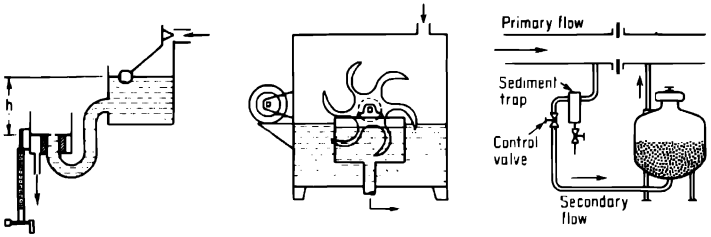
4. The two systems described on page 416 for dissolving and feeding solutions of fluorspar require, by means of solution feeders, the accurate feeding of alum solution into a tank containing fluorspar. The amount of alum solution delivered by these feeders not only controlled the quantity of fluorides dissolved from the fluorspar but also was used to suspend the resulting gypsum and separate it from the powdered fluorspar.

Solution feeders are devices for measuring and delivering a specific volume of liquid during a given time interval. The measuring function is accomplished by the automatic filling of a space in the feeder head with the liquid and then discharging it on the next cycle. This space can be in a pump cylinder, behind a diaphragm, in a series of buckets attached to a rotating wheel, or the difference in level in a tank. The most important characteristic of these devices is the invariable quantity of solution delivered during each time interval. Many so-called feeders (such as the flow from a restricted faucet or through an orifice plate attached to a container of liquid where the head on the orifice varies) are entirely unsuitable for fluoride feeding because of the wide variations in flow.

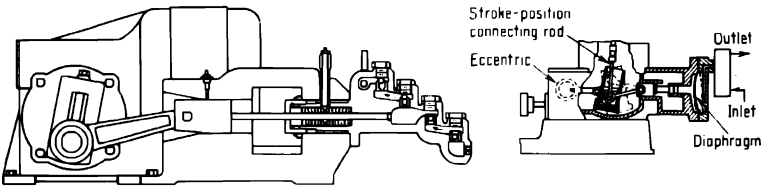
There are essentially four different types of satisfactory solution feeders available: diaphragm, piston, rotating cup, and decanting arm. The operating principles of all of these are illustrated in Figs. 10 and 11.

The most widely used solution feeders in the waterworks industry are the diaphragm types. The diaphragm, made of flexible rubber, plastic, or thin metals, is actuated (as shown in Fig. 12) either by a reciprocating plunger attached directly to the diaphragm or indirectly by means of periodically varying the pressure on a confined volume of hydraulic fluid. The reciprocating motion of the piston is obtained from either a slowly rotating cam or a crank.

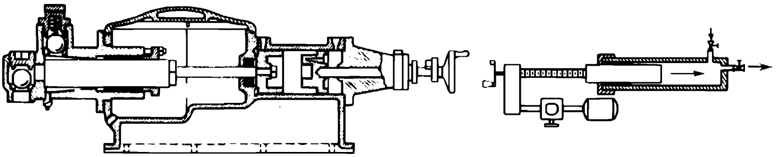
Variation in the capacity or the rate of feeding a solution is obtained by changing the speed of operation (depending on the motor speed, relative sizes of driven and drive pulleys, arrangement of gear reducers, and the like) and by varying the length of the stroke. The designs for varying the length of stroke differ widely and in many cases are the distinguishing characteristic of a particular feeder. Diaphragm feeders are ideally suited for medium-pressure service up to about 125 psi. They should not be used, however, against pressures less than about 5 psi and particularly should never be used against a vacuum, such as that obtained in the suction side of a pump. A constant positive pressure on the discharge is a guarantee of their continued accuracy. Some feeders are equipped with spring- or rubber-loaded discharge valves that assure the maintenance of such positive



Head Tank Paddle Wheel Pot Feeder



Positive-displacement Plunger Pump Positive-displacement Diaphragm Pump



Fluid-driven Pump Syringe

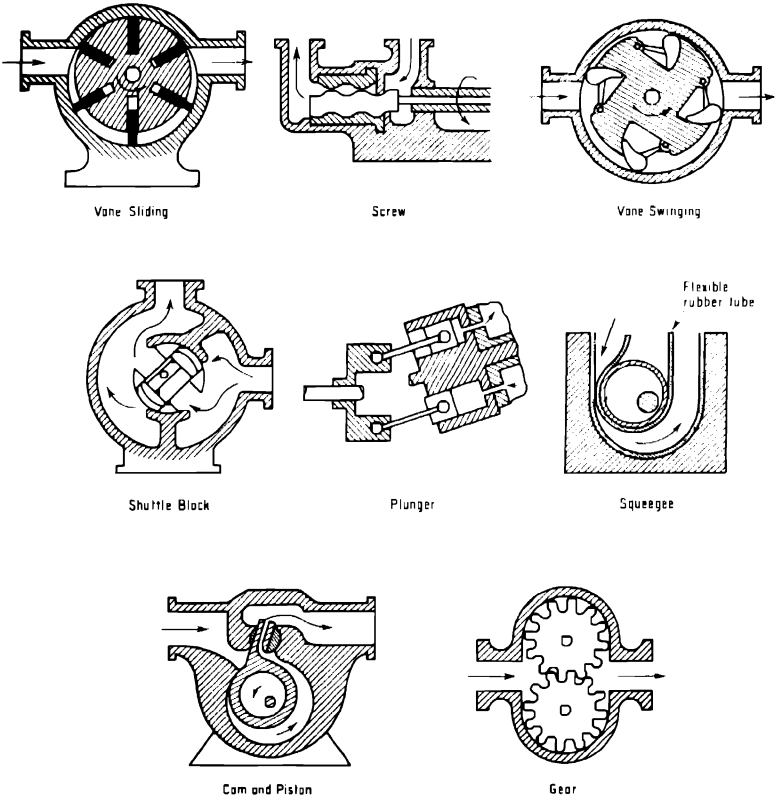
Fig. 10 Types of solution feeders for fluorides.

pressures. Negative suction heads should not ordinarily exceed about 4 ft and should remain constant.

Diaphragm and piston-type feeders are driven by almost any source of power which can impart a reciprocating motion to the piston. These include electric motors of various standard speeds, belt drives from shafts driving water pumps, and other rotating machinery in a water plant; gasoline motors; hydraulic or pneumatic pistons, with the energy obtained either from an auxiliary water pump or air compressor or from the pressure in the line carrying the water to be treated; or solenoids periodically energized by a timer or contactor actuated by a water meter or other pacing mechanism. The principal characteristic of such prime movers is that they are operated at a constant speed to produce a uniform solution delivery or at a speed proportional to the quantity of water to be treated or at the rate required by a fluoride transducer.

The piston or plunger pump (Fig. 13) is similar to the diaphragm type except that the piston directly displaces the quantity of solution to be fed. By reducing the diameter of the piston or the length of the stroke, very minute quantities of solution can be accurately fed. The length of the stroke is usually controlled by an adjustment of the crank arm or by limiting the length of contact against a rotating cam. Such adjustments can usually be made with the feeder running. As shown in Table 12-6, some plunger feeders can deliver accurately as little as 0.375 ml per minute. This type of feeder is driven by the same means as outlined for diaphragm feeders.

The delivery range of a particular piston or diaphragm feeder is usually limited between a fraction of its maximum delivery up to the maximum delivery at a particular maximum rotating speed, the minimum usually being between one-sixth and one-sixtieth of the maximum. In other words, if the maximum range is on the order of 10 to 1 ($\frac{1}{10}$) and the maximum delivery is 100 ml per min, then the minimum rate should not be less than about 10 ml per min. Although most feeder manufacturers provide means for reducing the minimum rate of delivery below the recommended rate,



Vane Sliding
Screw
Vane Swinging
Shuttle Block
Plunger
Squeegee
Cam and Piston
Gear

Fig. 11 Rotary-displacement-type solution feeders. *(USPHS.)*

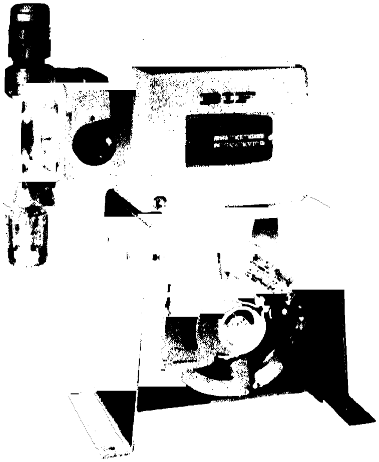


Fig. 12 Diaphragm-type solution feeder. *(B-I-F Industries, Inc.)*

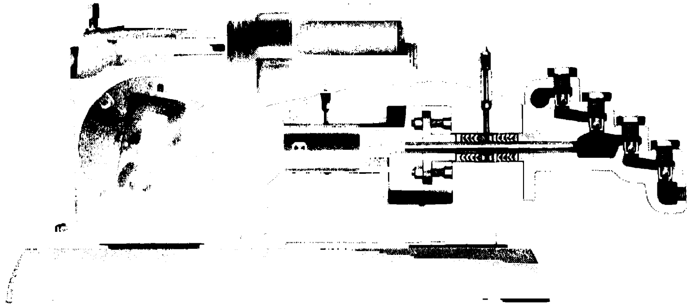


Fig. 13 Piston-type solution feeder. *(Milton Roy.)*

accuracy is markedly reduced in the lowest range. This reduction in accuracy is caused by check valves which either will not open or will leak at the lower rates. On the other hand, extremely high operating (rotating) speeds also markedly affect accuracy, because insufficient time is provided for the cylinder in the piston-type feeder or the space formed by the diaphragm to fill completely on the suction stroke.

The paddle wheel, or rotary dipper (also shown in Fig. 14), is widely used for accurate solution feeding. A constant-head device maintains the level of solution in a tank from which a series of cups attached to a partially submerged wheel lifts and discharges a constant volume of solution. Rate-of-feed variations are obtained by (1) changing the size of the dippers or cups,

Fig. 14 Rotary-dipper solution feeder. (*B-I-F Industries, Inc.*)

(2) adding or removing cups from the rotating wheel, (3) changing the speed of rotation, or (4) varying the proportion of the contents discharged from the full cups, the rest being returned to the tank. (A cutoff device is adjusted so that a portion or all of each full cup is discharged after each cup has emptied.) This type of feeder is intended for those installations in which the solution can be fed into another tank or basin or into a channel below the level of the feeder. It is not intended for use where feeding against any pressure.

Dry Feeders

Dry feeders are those devices which deliver a measured quantity of dry chemical during a particular interval of time. There are two basic types: volumetric feeders, which deliver a specific volume (cubic inches, cubic feet, quarts, pecks, bushels, barrels, and similar volumetric designations) of chemical material during a set time; and gravimetric feeders, which deliver a certain weight (ounces, pounds, grams, and the like) during a selected time interval. Generally, volumetric feeders can deliver smaller quantities than gravimetric feeders, but the principal differences in performance are: (1) volumetric feeders have an accuracy of from 3 to 5 per cent by weight as compared with 1 per cent for gravimetric feeders; (2) volumetric feeders are simpler and of less expensive construction; (3) gravimetric feeders are generally more readily adapted for recording the quantities of compounds fed and for automatic control. Gravimetric feeders are almost invariably used in the larger plants.

Many types of volumetric feeders can be converted to gravimetric types by attaching a weighing mechanism to the entire assembly. The delivery from such a feeder is then automatically controlled by the loss in weight resulting from the removal of some of the compound from the hopper. One of these is shown in Fig. 15.

Volumetric feeders are essentially a combination of a driving mechanism, a means for delivering a constant volume of dry compound, a hopper for holding the compound, and a chamber for dissolving the compound before discharge into the water supply.

The driving mechanism is almost invariably an electric motor, the speed of which has been reduced through gears or belt drives. Occasionally belts from other rotating equipment, such as from the shaft of a pump, are used as the driving mechanism.

The chemical-delivery mechanism is a convenient means for distinguishing one type of volumetric feeder from another. Almost every manufacturer has a different design for feeding chemicals volumetrically. These might be classified according to several types: rotating disk, oscillating pan, reciprocating screw, rotating roller, star wheel, vibratory pan, and combinations of these principles.

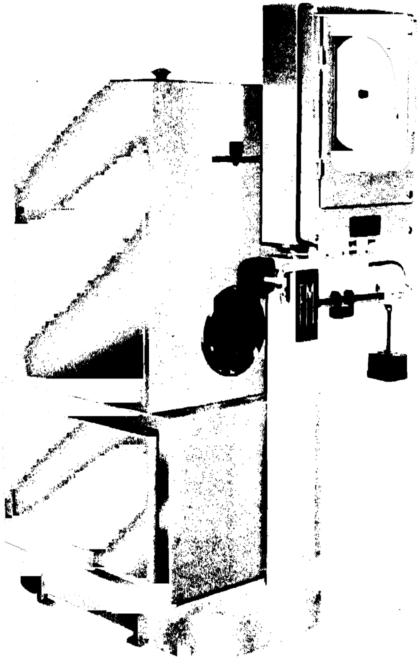


Fig. 15 Volumetric feeder converted to gravimetric operation. (*Wallace & Tiernan.*)

The rotating-disk feeders are probably the most widely used, particularly in the smaller plants. They are fitted with a horizontally rotating flat steel disk. The chemical to be fed flows from the hopper into the center of the rotating disk. A scraper removes a portion of the material as the disk slowly rotates. For very low rates, a groove is cut in the face of the disk, and material is removed from the groove by an appropriately shaped scraper. The widths of the grooves can be varied for different rates of delivery. Feed rates can also be changed by controlling the speed of rotation of disk and by adjusting the position of the scraper to govern the amount of material removed. Rates can be as little as 1 oz sodium fluoride per hour (75 per cu ft) up to 400 lb per hour.

Except for the vibratory-pan volumetric feeders, the others in this category are self-explanatory, mechanically actuated devices. Details on their construction and operation can be readily obtained from the manufacturers. The vibratory-pan feeder is a device for discharging a volume of chemical from a pan, chute, or trough made to vibrate electrically. A magnet is energized by means of a pulsating current (either ordinary alternating current or rectified, pulsating direct current). The rate is controlled by a rheostat, which determines the voltage and consequently the degree of movement of the trough. A wide range of sizes is available, the range of delivery being from 2 g per hour to 8,000 lb or more per hour. In water plants, however, only the smaller units might be used for fluoridation; the larger plants obtain much better accuracy with gravimetric feeders. Power consumption of this feeder is only 3 watts.

Gravimetric Feeders

Gravimetric feeders deliver chemicals at a constant weight rather than at a constant volume during a given period of time. Because of their great accuracy they should be used for feeding fluoride compounds wherever possible. Only when the minimum demand for chemicals is less than about 10 lb per hour should other types of feeders be considered. Gravimetric feeders are also quite readily adaptable for recording quantities of chemical feed and for automatic control. Another advantage is that a constant weight will be fed even if the bulk density of the compound has changed.

The chemical must be continuously weighed because control of these feeders is based entirely on weight. Such control is accomplished in two basic ways. In one the container (storage bin or hopper) is continuously weighed, and the rate of loss in weight of the material in the hopper is automatically maintained by prior selection of the rate of feed. The discharge is so regulated that the material left in the hopper follows a linear reduction in weight. In the other type, a section of a moving belt carrying the compound is continuously weighed. The flow of compound onto the belt is controlled by the deviations from a desired preset rate of discharge.

The error in feeding in this type of feeder is generally less than 1 per cent. The minimum delivery is 10 lb per hour with a range of feed on the order of 100 to 1, while some models can deliver more than 2 tons per hour.

EFFECTS OF FLUORIDES ON WATER-PLANT EQUIPMENT AND THE DISTRIBUTION SYSTEM

The addition of fluorides to water is undertaken solely for the purpose of protecting teeth from dental decay. Since this practice was instituted in 1945, some interesting side effects and some advantages and disadvantages to water-plant operation have occurred. None of these involve physiological benefits; all are related to the equipment used for the treatment and distribution of water.

Leaks. It is sometimes difficult to determine whether water appearing on the ground surface comes from a leak in the distribution system or from groundwater. In order to positively determine whether a leak has occurred without the laborious task of digging down to the main, it is only necessary to analyze a sample of the water for fluoride. When the community water supply is fluoridated, the source of this standing water is readily identified.

Tracing Possibilities. Information necessary for the efficient operation, maintenance, and expansion of distribution systems includes data on water velocities, directions of flow, condition of mains (roughness coefficients), position and presence of valves, and detention times in basins and reservoirs. Such data are sometimes very difficult to obtain without elaborate calculations. Much can be learned by the incorporation of study related to the start of fluoridation in a community. By selecting critical points for sampling and knowing exactly when fluoridation will begin, the first appearance of fluorides at these points can easily be established through sampling.

Scaling. Incrustants in the form of calcium or magnesium fluorides or calcium or magnesium silicofluorides are formed occasionally in the pipelines, tanks, eductors, and pumps handling concentrated fluoride solutions prior to the point of fluoride application to the water supply. Scaling in the distribution system has never been known to have been caused by water treated by such fluoride compounds. The severity of scaling at the plant is a function of the type of fluoride compounds formed, the amount handled, the hardness of the water, and its velocity or degree of agitation at a given point.

Scaling can be eliminated by removing the original cause, i.e., either by reducing the amount of calcium or magnesium by softening the water prior to making the fluoride solutions or by sequestering these elements with hexametaphosphate solutions. Where relatively smaller quantities of makeup water are required (as for instance, the water used in a sodium fluoride saturator tank), it may be more economical to soften the water in a small, salt-regenerated pressure softener. Where large quantities of water are required (in the dissolving chamber of a dry feeder), polyphosphate solutions (made from Calgon, Calco 918, or Micromet) can be economically used. The amount to be fed (on the order of five to ten times the hardness) is determined by experience.

Corrosion. The addition of the optimum quantity of fluorides to water supplies has never caused an increase in the corrosive properties of the water so treated. The concentrated fluoride solutions prior to feeding are corrosive, however, and materials in the feeding and piping equipment should be selected accordingly. Generally, the stainless steels and plastics furnished by the manufacturers of the equipment have been entirely satisfactory in overcoming this problem.

SAFE HANDLING OF FLUORIDE COMPOUNDS

Waterworks operators who handle fluoride compounds must be trained to realize the toxic nature of these compounds and to avoid accidental exposures. Such exposures can be caused by accidental dumping of the material, by inhalation from dust or vapor in the atmosphere, or by exposures which result in acid burns. No dangerous exposures have been reported, but the possibilities should never be minimized.

The possibility of excessive exposure in water-treatment plants is very unlikely. Fluoride-feeding equipment is generally designed so that hoppers require refilling no more often than once a day. Inasmuch as maximum exposure is more likely to occur during such filling operations, at least it will be limited to only a few minutes a day.

Nevertheless full advantage should be taken of the procedures and equipment available to protect workmen from possible hazardous exposures. Considerable margins of safety can be obtained by choosing less hazardous fluoride compounds, by equipping feeders and hoppers with safety appurtenances, and by providing personal safety equipment.

Of the powdered fluoride compounds, fluorspar is by far the safest from a toxicological point of view. The solubility of calcium fluoride is so low that the amount absorbed by the digestive system is considerably less than from a more soluble compound such as, for instance, sodium fluoride. Safety with dry powdered chemicals can also be increased by selecting a grade or mesh size which will produce no dust and which therefore cannot be inhaled. The crystalline grade of sodium fluoride, for example, contains very few dust-forming particles and should be used in preference to the powdered grades whenever possible. Liquid fluorides (hydrofluosilicic acid) cannot produce dust.

However, if dust-free materials cannot be used (sodium silicofluoride has an enormous economic advantage over some of the other fluoride compounds but cannot be obtained in the larger dust-free mesh sizes), then some provision must be made to suppress the dust hazard. In smaller plants, little danger to the operators is involved if reasonable care is used in handling the compounds so that the least amount of dust is produced. The greatest possibilities of exposure occur in the larger plants, where barrels of the fluoride compounds are dumped into hoppers, the openings of which are at or near the floor level. When the fluorides arch in these barrels and then suddenly empty, a cloud of dust may be formed. In all such cases the hoppers should be equipped with dust exhaust systems.

In some of the smaller plants, a bag loader is used on dry feeders. With this device it is possible to dump automatically the 100-lb bags into the hopper when the door holding the bag is closed. The empty bag is removed when the next filling takes place. A dust-removal or control system is not necessary with this device.

In all cases the operators should wear gloves and masks approved by the Bureau of Mines for protection against toxic dusts.

Hydrofluosilicic acid is much less hazardous but should nevertheless be treated with respect. Fortunately, it is seldom necessary to handle it in any way other than pumping it through pipes or tubing. If at all possible, it should never be diluted before feeding. Generally, this acid can be fed directly from a shipping container or pumped directly from a storage tank. The storage tank is filled from tank trucks or railway tank cars.

The greatest care should be taken when repairing pipelines and pumps which contain this acid, particularly in protecting the hands and eyes. Goggles, face masks, rubber gloves, and boots should be worn. A copious amount of flowing water should be immediately available for flushing the eyes and for rinsing the hands and other parts of the skin.

The rooms in which acid equipment is housed should be continuously ventilated and the spent air exhausted to the outdoors. All vents on tanks should terminate outdoors in a gooseneck fitting.

In handling any fluoride compound, scrupulous cleanliness should be continuously maintained. All spills should be immediately hosed down and mopped. Acid spills can be neutralized with lime water. Thorough hand washing should be routinely practiced after each loading, and daily showers should be taken if the loadings are prolonged.

DEFLUORIDATION OF WATER

When water supplies contain excessive fluorides, the teeth of most of the people using such waters become mottled with a permanent black or gray discoloration of the enamel. Children who have been using water containing 5 ppm or more of fluorides are all invariably afflicted with this defect; for many, the enamel becomes so severely pitted that eventually they lose their teeth.

Water-treatment plants for removing such excessive fluorides have been in operation for over 22 years. Recently the children in communities served by such treated supplies were reexamined. The widespread fluorosis previously observed among children brought up on defluoridated water had been arrested, and no severe cases were found.

There are over 4 million persons in the United States living in 1,200 communities where the public water supplies contain excessive fluoride. In 264 of these communities the fluoride levels are at least three times the optimum amounts (the optimum level is the one deemed best for inhibiting tooth decay; see page 409). The U.S. Public Health Service *Drinking Water Standards* suggests that fluoride levels of two times the optimum concentration constitutes grounds for rejecting the supply.

Despite the obvious need for such water-treatment plants, and the demonstrated benefits resulting from their use, only 14 plants have so far been built. This lack of acceptance of methods for preventing fluorosis is probably due to the alleged excessive costs of treatment plants, the cost of operating such plants, and the complexity of the operating procedures. Actually the experience gained so far in the design, construction, and operation of various processes for defluoridating water indicates that these allegations are no longer tenable.

At present, three defluoridation methods have proved practicable under varying conditions of raw-water quality and availability of treatment chemicals. These methods involve the use of activated alumina, bone char, or magnesium compounds. The first two methods employ insoluble, granular media which remove the fluorides as the water percolates through them. The media are periodically regenerated by chemical treatment when they become saturated with the fluoride removed from the water. In the third method, the fluorides are removed along with the magnesium which might be added in the form of a lime. Both the fluorides and the magnesiums are subsequently removed through the use of settling basins and then discarded.

Activated alumina is being used at the municipal Bartlett, Texas, plant and at the Air Force base at Clovis, New Mexico. This material is available from several aluminum manufacturers in various mesh sizes of granules and degrees of purity. Activated alumina is commonly used as a desiccant, particularly in air-conditioning equipment. For defluoridating, it is used in mesh sizes between 28 and 48. In 1969 it cost 20½ cents per pound and weighs, in place, 50 lb per cubic foot. The Bartlett plant (Fig. 16) contains 500 cu ft of alumina in a standard circular steel filter tank 11 ft

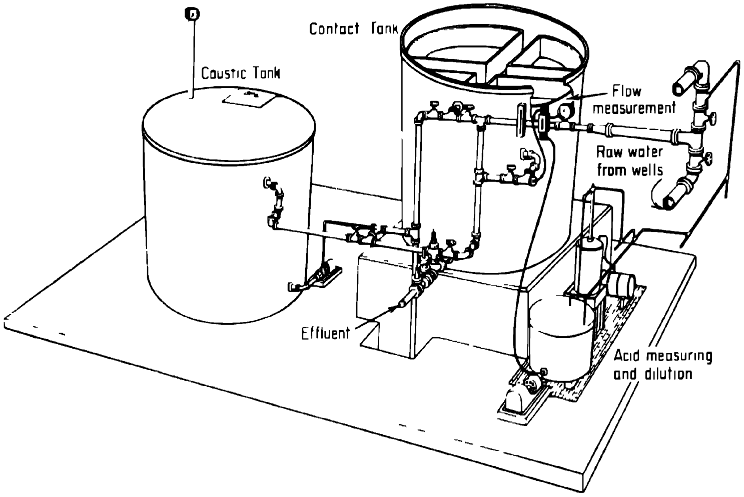


Fig. 16 Defluoridation plant at Bartlett, Texas. *(USPHS.)*

in diam and 11½ ft high. The plant is capable of treating 400 gpm of Bartlett well water and was designed to reduce the fluoride from 8.0 ppm to an average of 1.0 ppm.

When about 1 million gal of water have been treated, the alumina becomes saturated with fluorides and must be regenerated. Regeneration of the activated alumina consists of various steps designed to remove, by backwashing, the accumulated solids that have been strained from the water; to remove (by means of a weak caustic solution) the fluorides that have been absorbed by the medium; and to neutralize the residual caustic with weak acid and water rinses. At present, the caustic solution is applied countercurrently, so that one operation combines the backwashing step (saving the treated water formerly used for this purpose) and the caustic application. After a rinse to reduce the alkalinity as much as practicable, a weak (0.05 normal) sulfuric acid rinse is applied until the alkalinity of the wastewater is low enough to make the effluent usable. The total amount of raw water used for regeneration is 68,500 gal.

The equipment for the Bartlett plant cost $11,360 in 1951, including installation. The alumina cost an additional $4,000. The building was furnished by the city. Operation started in March, 1952.

The plant at Bartlett is a gravity type, in that the contact tank is open to the atmosphere. The plant at Britton, South Dakota, on the other hand, is a pressure type, in which the medium is confined in a heavy steel tank designed to withstand the pressure of water in the distribution system. The water at Britton is pumped from any of three wells through the defluoridation tank and directly into the distribution system. The tank contains 300 cu ft of bone char, which at present is used in the United States only at this plant. The fluorides are reduced from 6.7 ppm to an average of 1.5 ppm. The char is 30 to 50 mesh and is ordinarily used in sugar refineries for decolorizing the sugar syrup.

After treating about 1 million gal, the bone char becomes saturated with fluoride and must be regenerated. This consists of backwashing to remove the accumulated sand and them pumping a 1% solution of caustic soda through the medium. After the fluorides have been removed by the caustic, the excess caustic remaining in the bone char must be removed. This is done by rinsing the bed with raw water until the pH of the effluent approaches that of the raw water. No treated water is used for regeneration, while about 44,000 gal of raw water is used for rinsing.

Construction of this plant was completed and operation was started in November, 1948, with a synthetic hydroxy apatite for a medium. This material was abandoned during February, 1953, because of excessive (42 per cent per year) losses due to attrition. The cost of the equipment for the plant in 1947 was $12,245 including the bone char. Bone char of the type suitable for this purpose in 1968 cost 12½ cents per lb. At this price a complete charge of 300 cu ft costs $1,500. Chemical costs for regeneration amount to about $27 per million gal.

No plants have yet been built specifically for fluoride removal using the magnesium process. There are, however, several softening plants in Ohio, Indiana, and Illinois that incidentally remove small amounts of fluoride along with the magnesium. This combination of functions, using the same equipment and treatment chemicals, would make the cost of defluoridation lower than that of any other process. On the other hand, the initial cost of building such plants is considerably higher, and chemical and sludge handling is more difficult.

The problems related to the operation, control, and maintenance of defluoridation plants are no more difficult than those encountered in conventional water-treatment plants. Experience has shown that the employees of water systems previously involved only in well-pump operation and meter reading could become capable defluoridation-plant operators after adequate training. The equipment required for these defluoridation plants is a collection of standard water-treatment plant items, and their cost and complexity are identical to those of softening or ion-exchange plants. In addition, the operating costs of such plants are comparable to the costs of defluoridation plants.

The removal of excessive fluorides from public water supplies to prevent dental disfigurement, loss of teeth, and increased cost of dental care is a sound economic investment. The results obtained make defluoridation more justifiable than many other water-treatment processes.

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Radioactivity

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Radioactive materials have been identified in water for a long time. Until 1945, however, when the fission reaction was demonstrated with its release of fantastic quantities of energy and the production of a large number of radionuclides unknown to man, most measurements were made of the naturally occurring radionuclides. These naturally occurring radionuclides, particularly those of the uranium series, were ascribed curative properties, and many early bottled water supplies boasted of their radium content. Similarly, these materials were suggested or used for the measurement of the movement of specific waste streams.[1,2] Additional literature on the use of tracers for this purpose has been identified.[3]

Progress in the use, handling, and disposition of radioactive materials during the past two decades has made certain radionuclides household words. Who has not heard of iodine 131, strontium 90, cesium 137, or radium 226? This progress, which has led to the use of atomic energy for peaceful purposes including the production of electricity, has focused additional attention on water. In the atomic-energy field, water is used as a coolant, as a moderator, and as a medium for the transport or removal of radioactive waste materials. In the sections that follow, treatment to meet these new requirements will be considered, and the techniques and efficiency of existing processes for the removal of these contaminants will be indicated. In addition, reference will be made to permissible levels of specific radionuclides in water promulgated by international and national bodies.

WATER AS MODERATOR AND COOLANT

Information on the characteristics of water used for cooling and moderation was obtained from 12 power reactor stations.[4] These results are summarized in Table 13-1.

TABLE 13-1 Coolant and Moderator Water Chemical Characteristics

Characteristic	Range of values
Conductivity, μmhos	$<$ 0.1–5
Total solids, mg/l	$<$ 0.5–2.0
Turbidity, mg/l	1.0–10
pH	4–10
Chloride, mg/l	0.01–1.0
Fluoride, mg/l	0.1–0.15
Boron, mg/l	0–100
Silica, mg/l	0.25–3.0
Oxygen, mg/l	0.005–0.2
Hydrogen, mg/l	15–60
Gross iodine, μCi/ml	10^{-4}–35

Water of these characteristics is produced following treatment by evaporation, degasification, and demineralization with mixed-bed ion exchangers. After passage through the coolant system, the coolant is contaminated from contact with the reactor and fuel surfaces and with radionuclides released from damaged or leaking fuel elements. A variety of radionuclides have been encountered in coolant waters as shown in Table 13-2.

Purity of the cooling water is maintained by passing the coolant through filters and mixed-bed ion exchangers. Where necessary, gas stripping of inert gases (xenon and krypton) is also practiced.

Waters from fuel storage (canal water) receive treatment to minimize the exposure of personnel to radiation. Treatment consists of passing a continuous fraction of the canal water through filters and mixed bed ion exchangers. In one instance, a canal contaminated with iron bacteria was successfully cleaned with 5% hydrogen peroxide.

Spent resins from all operations are usually sluiced to tanks for storage and decay before packaging with cement or other material in drums for offsite disposal, generally at authorized land burial sites.

TABLE 13-2 Radioactive Contaminants in Cooling Water

Source	Nuclides identified*
Corrosion products	Fe^{59}, Co^{58}, Co^{60}, Mn^{54}, Mn^{56}, Cr^{51}, Hf^{181}, Zr^{95}, Na^{24}, Cu^{64}, No^{65}, Zn^{65}, Zn^{65m}, Mo^{99}, Tc^{99m}, Sb^{124}, W^{187}, P^{32}, Ag^{110m}, Ta^{182}
Radicals	NO_2, NO_3, or NH_3, with nitrogen is N^{13}, N^{14} or N^{16} O^{18}, and F^{19} as compounds
Fission products from failure or contamination of cladding material	Xe^{133}, Xe^{135}, Kr^{87-88}, Sr^{89-92}, Br^{82-85}, Rb^{88}, Tc^{99}, Mo^{99}, $I^{131-135}$, $Cs^{136-139}$, $Ba^{139-140}$, Zr^{95}, Zr^{97}, etc.
Activation product	Np^{239}

*Since this was written, the conventional representation for radionuclides has been changed to ^{60}Co, etc.

REMOVAL OF RADIONUCLIDES BY WATER-TREATMENT PROCESSES*

Radioactive materials enter surface streams as discharges from atomic-energy installations, from users of radionuclides for beneficial purposes, and as fallout with precipitation or runoff. The water-treatment plant is the last point of control between the release of this material and the ultimate consumer of water. Thus, considerable effort has been expended in identifying the degree of removal to be expected through the use of various treatment processes for the wide range of radionuclides released to the water environment. Results to be expected through the use of conventional and modified processes and the experience gained with full-scale plant operations will be reported. These results, however, do not necessarily apply to other situations. Consideration must be given to the chemical form of the radionuclide, the pH of treatment, and the age of the mixture where mixed fission products are being treated. These factors all influence uptake markedly, and it is well to carry out preliminary jar-test studies prior to initiating large-scale treatment.

Conventional Treatment

Conventional treatment consists of coagulation, sedimentation, rapid- or slow-sand filtration, lime-soda ash softening, and ion exchange.

(1) *Coagulation and Settling.* Coagulation involves the formation of chemical flocs that bring together finely divided suspended matter. The addition of coagulants will result in the precipitation of some of the soluble

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*Much of the material under this heading is taken from Chap. 8, Removal by Water-treatment Processes, of "Low Level Radioactive Wastes" by Conrad P. Straub, pp. 155–202, available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., 1964.

TABLE 13-3 Removal of Soluble Radioactivity by Chemical Coagulation

Nuclide	Chemical form	Chemical group	Number of tests	Activity range counts/min-ml	pH range		Removal		Reference	Coagulants used	Coagulant dose, mg/l
					Initial	Final	Average, %	Range, %			
Cs^{137}—Ba^{137m}	Cl^-	IA IIA	27	19–17,390	7.5–7.8	6.5–7.8	0.5	0–37	5	$Al_2(SO_4)_3$, $FeCl_3$, $FeSO_4 \cdot 7H_2O$	17.1, 34.2, and 103
Sr^{89}	Cl^- or NO_3^-	IIA	54	212–25,950	7.7–7.9	7.5–8.0	3	0–15	5	$Al_2(SO_4)_3$, $FeCl_3$, $FeSO_4 \cdot 7H_2O$	17.1, 34.2, and 103
Sr^{89}		IIA	12	....	....	....	38	5–58	6	Variable amounts of clay added	
$Sr^{89,90}$		IIA	....	....	....	6.8–7.0	3	2–5	9	Alum, $Fe_2(SO_4)_3$ and other treatments	10 as Fe and as Al
Ba^{140}—La^{140}	Cl^-	IIA IIIA	81	42–17,150	7.4–7.6	7.2–8.2	59	1–84	5	$Al_2(SO_4)_3$, $FeCl_3$, $FeSO_4 \cdot 7H_2O$	17.1, 34.2, and 103
			54	42–5,520	7.4–7.6	6.6–7.9	44	19–59	5	$Al_2(SO_4)_3 \cdot FeCl_3$, $FeSO_4 \cdot 7H_2O$	17.1, 34.2, and 103
			54	44–8,070	7.4–7.6	7.2–7.8	52	27–72	5	$Al_2(SO_4)_3$, $FeCl_3$, $FeSO_4 \cdot 7H_2O$	17.1, 34.2, and 103
Ba^{140}—La^{140}	Cl^-	IIA IIIA	4	17,500–46,200	7.7–7.8	....	64	58–71	7	$CaCO_3$ and $FeCl_3$ or alum	50–100
Sc^{46}	Cl^-	IIIA	27	163–24,300	7.2–7.8	6.4–8.0	89	62–98	5	$Al_2(SO_4)_3$, $FeCl_3$, $FeSO_4 \cdot 7H_2O$	17.1, 34.2, and 103
			27	326–20,060	7.6	7.0–7.8	92	62–99 +	5	$Al_2(SO_4)_3$, $FeCl_3$, $FeSO_4 \cdot 7H_2O$	17.1, 34.2, and 103
			27	202–26,100	7.5–7.9	6.9–8.2	91	69–99 +	5	$Al_2(SO_4)_3$, $FeCl_3$, $FeSO_4 \cdot 7H_2O$	17.1, 34.2, and 103
Y^{91}	Cl^-	IIIA	54*	188–4,166	7.5–7.6	6.0–7.6	90	40–99	5	$Al_2(SO_4)_3$, $FeCl_3$, $FeSO_4 \cdot 7H_2O$	17.1, 34.2, and 103
			81*	367–20,860	8.1	7.8–10.2	92	56–99 +	5	$Al_2(SO_4)_3$, $FeCl_3$, $FeSO_4 \cdot 7H_2O$	17.1, 34.2, and 103
			81*	202–21,450	7.8–8.0	7.6–8.4	86	48–99	5	$Al_2(SO_4)_3$, $FeCl_3$, $FeSO_4 \cdot 7H_2O$	17.1, 34.2, and 103
			81†	406–21,500	7.8	7.5–9.1	75	1–98	5	$Al_2(SO_4)_3$, $FeCl_3$, $FeSO_4 \cdot 7H_2O$	17.1, 34.2, and 103
			81†	222–21,500	7.1–8.4	7.4–9.5	73	33–98	5	$Al_2(SO_4)_3$, $FeCl_3$, $FeSO_4 \cdot 7H_2O$	17.1, 34.2, and 103
Zr^{95}—Nb^{95}	Oxylate complex	IVB VB	54	186–27,200	7.4–7.6	6.4–7.9	80	2–99	5	$Al_2(SO_4)_3$, $FeCl_3$, $FeSO_4 \cdot 7H_2O$	17.1, 34.2, and 103
Zr^{95}—Nb^{95}	Oxylate complex	IVB VB	4	29,800–78,000	8.4–8.7	....	88	76–99	7	$CaCO_3$ and $FeCl_3$ or alum	40–400
P^{32}	PO_4^{-3}	VA	27	228–17,625	7.6	6.4–7.8	96	68–99 +	5	$Al_2(SO_4)_3$, $FeCl_3$, $FeSO_4 \cdot 7H_2O$	17.1, 34.2, and 103
P^{32}	PO_4^{-3}	VA	12	....	....	....	97	63–99 +	6		
Cr^{51}	Cl^-, metal	VIB	54	5–758	6.7–7.3	5.3–7.8	6	0–60	5	$Al_2(SO_4)_3$, $FeCl_3$, $FeSO_4 \cdot 7H_2O$	17.1, 34.2, and 103

Mo^{99}	MoO_3	VIB	54	84–10,085	7.6	7.0–8.2	10	0–60	5	$Al_2(SO_4)_3$, $FeCl_3$, $FeSO_4 \cdot 7H_2O$	17.1, 34.2, and 103
W^{185}	Tungstate	VIB	54	233–28,290	7.5–7.9	6.6–8.4	46	1–96	5	$Al_2(SO_4)_3$, $FeCl_3$, $FeSO_4 \cdot 7H_2O$	17.1, 34.2, and 103
			81	198–22,490	8.0–8.1	7.5–8.4	36	4–91	5	$Al_2(SO_4)_3$, $FeCl_3$, $FeSO_4 \cdot 7H_2O$	17.1, 34.2, and 103
Re^{186}	Metal	VIIB	54	95–15,230	7.6	7.2–8.0	6	0–29	5	$Al_2(SO_4)_3$, $FeCl_3$, $FeSO_4 \cdot 7H_2O$	17.1, 34.2, and 103
I^{131}	Iodide	VIIA	27	239–25,060	7.6	7.2–7.8	20	0–44	5	$Al_2(SO_4)_3$, $FeCl_3$, $FeSO_4 \cdot 7H_2O$	17.1, 34.2, and 103
I^{131}	Iodide	VIIA	12	....	....	....	3.9	0–12	6	$Al_2(SO_4)_3$, $FeCl_3$, $FeSO_4 \cdot 7H_2O$	17.1, 34.2, and 103
I^{131}	Iodide	VIIA	4	13,000–24,800	6.3–7.7	....	42	26–63	7	$CaCO_3$ and $FeCl_3$ or alum	50–200
I^{131}	Iodide	VIIA	19	2,000‡	....	5.4–7.6	0.8	0–10	8	Variety of chemicals	
Ru^{103}	Cl^-	VIII	27	196–24,960	7.3–7.6	6.9–8.2	77	43–96	5	$Al_2(SO_4)_3$, $FeCl_3$, or alum	17.1, 34.2, and 103
Co^{60}	Cl^-	VIII	2	45,900–49,400	7.6–8.2	....	16	8–23	7	$CaCO_3$ and $FeCl_3$ or alum	50–100
Pr^{142}	Pr_2O_3	La series	27	102–12,050	7.2	7.4–8.0	96	83–99 +	5	$Al_2(SO_4)_3$, $FeCl_3$, or alum	17.1, 34.2, and 103
Ce^{144}—Pr^{144}	Cl^-	La series	27	244–30,510	7.4–7.6	7.2–8.4	91	28–99 +	5	$Al_2(SO_4)_3$, $FeCl_3$, or alum	17.1, 34.2, and 103
$Ce^{141,144}$—Pr^{144}	Cl^-	La series	4	41,000–55,800	7.1–7.6	....	98	96–99 +	7	$CaCO_3$ and $FeCl_3$ or alum	50–200
Pm^{147}	Cl^-	La series	27	136–19,040	7.4–7.6	7.0–8.2	87	4–99 +	5	$Al_2(SO_4)_3$, $FeCl_3$, or alum	17.1, 34.2, and 103
Sm^{153}	Sm_2O_3	La series	54	148–20,870	7.4–7.6	5.8–8.0	91	44–99 +	5	$Al_2(SO_4)_3$, $FeCl_3$, or alum	17.1, 34.2, and 103
Fission-product mixture	Ba 5% Ce 27 Cs 1 Ru 3 Sr 17 TRE 4 Other 3		1	22,200	8.5	....	89	....	7	$FeCl_3 + CaCO_3$	170–240
Fission-product mixture	Ba 5% Ce 5 Cs 50 Ru 16 Sr 10 TRE 10 Other 4		1	22,200	8.5	....	55	51–59	7	$FeCl_3 + CaCO_3$	100–400

*$Ca(OH)_2$ used as alkaline agent.

†Na_2CO_3 used as alkaline agent.

TABLE 13–4 Coagulation and Settling Results (Jar-test Studies)

Nuclide	Clay added,[1] mg/l	Coagulant added,[2] g/gal	Final pH	Removal, %
Cs^{137}-Ba^{137m}	0	1	....	0–6
	100	1	....	35–65
Sr^{89}	0	1.5[3]	6.7–7.8	0–6
	100	0.5–6	6.7–10.7	0–51
Cd^{115}	0	1	....	40–60
	100	1–5	....	60–95
Ba^{140}-La^{140}	100	1–6	7.5–8.2	28–84
Sc^{46}	100	1–6	6.5–8.2	66–98
Y^{91}	0	1.5[3]	6.8–7.1	83–93
	100	1–6	7.0–10.2	34–99
Zr^{95}-Nb^{95}	0	1–5	....	70–98
	100	1	....	95–99
P^{32}	100	0.5–1.5[3]	6.8–8.8	97–99
Cr^{51}	100	1–6	7.6–8.8	73–98
W^{185}	100	1–6	7.5–8.4	5–91
I^{131}	100	0.5–2[3]	6.9–9.0	0–10
Ce^{144}	0	1–1.5[3]	7.2–7.8	81–94
	100	0.5–2.5[3]	7.0–7.8	85–96
Fission-product mixture 1[4]	100	1–3[3]	7.2–8.8	61–84
Fission-product mixture 2[5]	0	1–5	4.3–10.2	9–71
	100	1–5	4.3–10.2	12–73
Fission-product mixture 3[6]	0	10	9.9–10.0	46

[1] Local clay was added.

[2] Coagulant includes alum, ferrous sulfate or ferric chloride, lime, soda ash or sodium hydroxide, and sodium silicate.

[3] No sodium silicate added. Where added, sodium silicate equals 40 per cent primary coagulant dose.

[4] Iodine dissolver solution.

[5] Synthetic mixture containing fission products in the same ratios assumed to be present 30 days after an underwater detonation.

[6] Three-year-old fission-product mixture.

constituents in the waste as metal hydroxides. Results[5-9] for a wide variety of soluble radionuclides are summarized in Table 13-3. Coagulation is effective for the removal of most cations of valence 3, 4, or 5, including the rare-earths group, and is not effective for the removal of cesium, strontium, or barium—elements of groups 1 and 2. It is more effective in removing particulate associated radioactivity, as for example, radioactivity associated with the turbidity found in most surface waters. Setter and Russell[10] have shown that 97 to 100 per cent of the radioactivity associated with the particulate matter and 4 to 81 per cent of that associated with soluble material was removed in the treatment of rainfall samples contaminated by fallout.

TABLE 13-5 Removal of I^{131} by Auxiliary Processes

Turbidity	Dosage, mg/l			Final characteristics, mg/l[1]			Removals, %		Reference
	Alum	NaOH	Auxiliary chemical	pH	Alkalinity	Turbidity	Coagulation and settling	Coagulation, settling, and centrifuging	
103	25.7	38.9	5-15[2]	5.8-7.1	17-68	0-15	64-72	74-78	8
103	25.7	38.9	3.5[3]	7.1	65	0	38	56	8
17.3-274	25.7	38.9	0.12-3.8[4]	5.8-7.5	19-74	1-40	42-74	48-76	8
....	113.5	....	0.013-0.13[4]	6.0-6.9	.....	....	55-90	.....	7
....	247	....	0.13-1.1[4]	6.3	.....	....	90-92	.....	7
....	100.64[5]	....	0.13[3]	6.3	.....	....	95.5	.....	7

[1] Except for pH.

[2] Auxiliary chemical was activated carbon.

[3] Auxiliary chemical was copper sulfate.

[4] Auxiliary chemical was silver nitrate.

[5] Either 20 mg/l as iron or 100.64 mg/l as $Fe_2(SO_4)_3 \cdot 9H_2O$.

The removal of soluble radionuclides, those adsorbable on clay, may be enhanced by the addition of clay with the usual coagulants. The addition of 100 mg/l of clay increased removal of soluble radionuclides, as shown by the results in Table 13-4.

The data in Table 13-3 show that iodine is not effectively removed through the use of conventional coagulants. Removal could be improved markedly[8,11] by the addition of small amounts of copper sulfate, activated carbon, or silver nitrate along with the usual coagulants. The results of some of these studies are shown in Table 13-5.

Strontium is ineffectively removed by coagulation as shown in Table 13-3. Removal could be increased by raising the pH, increasing iron coagulant dosages, or by addition of sodium metaphosphate.[9,12,13]

Removal will be variable in the case of mixed fission products because such removal is dependent upon the presence or absence of specific radionuclides. As shown in Table 13-6, removals range from 46 to 89 per cent.

TABLE 13-6 Removal of Mixed Fission-product Isotopes by Coagulation and Settling

Mixture	Removal, %
Fission-product mixture 1[1]	61–84[5]
Fission-product mixture 3[2]	46
Fission-product mixture 4[3]	89
Fission-product mixture 5[4]	51–59

[1] Iodine dissolver solution.
[2] Three-year-old fission-product mixture.
[3] Iodine dissolver solution aged 30 days.
[4] Mixed fission-product waste containing Cs^{137}-Ba^{137m} and Ru^{106}-Rh^{106}.
[5] Clay also added.

(2) *Sand Filtration.* Except for removal by simple straining or by sorption on biological life contained in the *Schmutzdecke*, sand filters have been ineffective for removing radioactive materials. Their major function is to remove the radioactivity previously incorporated in floc. Both rapid- and slow-sand filters have been evaluated for their efficiency in removing radioactive materials.

(*a*) *Rapid-sand filters.* Table 13-7 shows that materials such as scandium, yttrium, and zirconium-niobium, probably present as colloids, were readily removed when passed through rapid-sand filters; other materials, such as strontium, cesium, and possibly tungsten, present in true solution, were not affected by passage through sand filters.

(*b*) *Slow-sand filters.* The studies of Eden, Elkins, and Truesdale[14] have been summarized in Fig. 1. These data show that under the particular circumstances investigated, cerium and plutonium were removed far more effectively than were iodine, ruthenium, and strontium. The rate

TABLE 13-7 Laboratory Sand-filtration Results

Nuclide	Initial activity, counts/min-ml	Volume passed, ml	pH of effluent	Removal, %	
				Range	Average
Cs^{137}-Ba^{137m}	800	500	8.3	10-70	50
Sr^{89}	2,700	750	8.3	1-13	4
Cd^{115}	1,200	500	8.1	60-99	95
Ba^{140}-La^{140}	1,300	750	7.6	39-99	74
Sc^{46}	1,500	750	8.3	94-99	96
Y^{91}	5,700	750	7.0	84-89	87
Zr^{95}-Nb^{95}	3,400	500	7.8	91-96	93
W^{185}	2,200	750	7.1	3-18	8

of release of retained radioactivity is also shown by the dotted lines in Fig. 1.

(3) *Lime-Soda Ash Softening.* Lime-soda ash treatment is used extensively for the softening of many hard waters. This technique, used under proper conditions, results in the removal of soluble Ba^{140}-La^{140}, Sr^{89}, Cd^{115}, Sc^{46}, Y^{91}, and Zr^{95}-Nb^{95}. It was not effective for the removal of soluble I^{131}, Cs^{137}-Ba^{137m}, and W^{185}. Treatment with lime and soda ash is most applicable for the removal of strontium. However, to accomplish this, increased quantities of chemical[15] are required as shown in Table 13-8. Increasing the stoichiometric chemical requirements threefold increased removals of strontium from 75 to 99.7 per cent.

(*a*) *Solids-contact softening.* Hoyt[15] described pilot-scale studies using a 1,000-gpd Spaulding-type precipitator for the removal of strontium. The removal of suspended solids from the precipitator effluent by either filtration or centrifugation increased removals of hardness and activity to 87 and 96 per cent, respectively, when 50 mg/l of excess lime-soda ash were added. This compares with laboratory removals of strontium at this chemical dose of 80.1 per cent (Table 13-8).

(*b*) *"Repeated precipitation" process.* As another means of increasing strontium removals, McCauley and Eliassen[16] suggest the use of the "re-

TABLE 13-8 Results of Lime-Soda Ash Treatment for Removal of Strontium

Treatment	Removal of activity, %
Stoichiometric	75.0
Excess lime-soda ash, 20 mg/l	77.0
Excess lime-soda ash, 50 mg/l	80.1
Excess lime-soda ash, 100 mg/l	85.3
Excess lime-soda ash, 150 mg/l	97.3
Excess lime-soda ash, 200 mg/l	99.4
Excess lime-soda ash, 300 mg/l	99.7

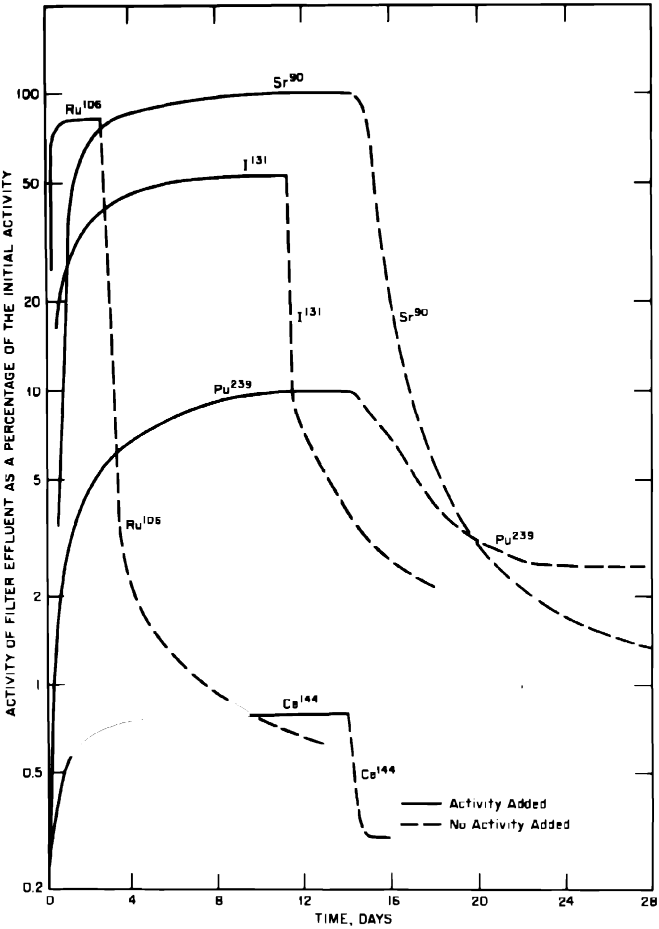

Fig. 1 Removal of radionuclides from water by slow-sand filtration.

peated precipitation" process, which provides for the addition and elimination of small quantities of calcium in several steps. It was estimated that ideally a 15-stage plant could increase strontium removals to 99.996 per cent if a 50 per cent efficiency for each stage is accepted.

(c) Hot-lime-soda ash softening. In hot-lime-soda ash softening at temperatures above 90 °C, the addition of enough soda ash to produce a 50 mg/l excess (as $CaCO_3$) over that amount required to react with noncarbonated hardness and enough lime to produce a pH of 9.8 to 10.0 *at*

equilibrium resulted in a reduction of calcium hardness to 5 mg/l or less and a simultaneous reduction of strontium activity by 95 per cent or more.

(4) *Ion Exchange.* Ion exchange, usually involving cation or base exchange, is used in the softening of municipal water supplies. Studies of tap water, with added soluble tracer amounts of W^{185}, Y^{91}, Sc^{46}, Sr^{89}, Ba^{140}-La^{140}, Cs^{137}-Ba^{137m}, Cd^{115}, and Zr^{95}-Nb^{95}, passed through various resins, yielded results given in Table 13-9. Data obtained with greensand are included for comparison.[17]

TABLE 13-9 Efficiency of Ion-exchange Materials in Removing Individual Nuclides

Nuclide	Removal, %			
	Cation exchange	Anion exchange	Mixed bed	Greensand
W^{185}	12-16	97.2-99.2	98.9	9
Y^{91}	86-93.1	94.2-98.5	97.6-98.7	75
Sc^{46}	95.7-97.2	98.8-99.0	98.5-98.7	96.4
Sr^{89}	99.1-99.8	5-7	99.95-99.97	99.8
Ba^{140}-La^{140}	98.3-99.0	36-42	99.5-99.6	96.3
Cs^{137}-Ba^{137m}	99.8	9	99.8	....
Cd^{115}	98.5	0	99.2	....
Zr^{95}-Nb^{95}	58-75	96.4-99.9	90.9-99.4	....

The cation-exchange materials evaluated included IR-120 (H^+ and Na^+ cycles) and a natural greensand (Na^+ cycle); the anion exchangers included Dowex-1 (OH^- and Cl^- cycles); and the mixed beds included IR-120 (H^+) plus Dowex-1 (OH^-) and IR-120 (Na^+) plus Dowex-1 (Cl^-). In water-treatment practice the effluent pH is of significance and should be near neutrality. From the standpoint of pH, the most satisfactory water-treatment effluents were those produced with Dowex-1 (Cl^-) and greensand.

Lacy and Lindsten[18] reported on the removal of specific radionuclides from tap water slurried with ion-exchange resin. Typical results are shown in Figs. 2 and 3. As shown in Fig. 2, increased removal occurs with an increase in slurrying time and concentration of resin. Marked differences in rates of removal are indicated by data in Fig. 3.

Nonconventional Treatment

Nonconventional processes studied, which can be utilized in conjunction with conventional water-treatment plants, include phosphate coagulation, the addition of metallic dusts, and the addition of clay materials.

(1) *Phosphate Coagulation.* Phosphate coagulation was investigated by Lauderdale,[19] with results shown in Table 13-10. As seen, removals of

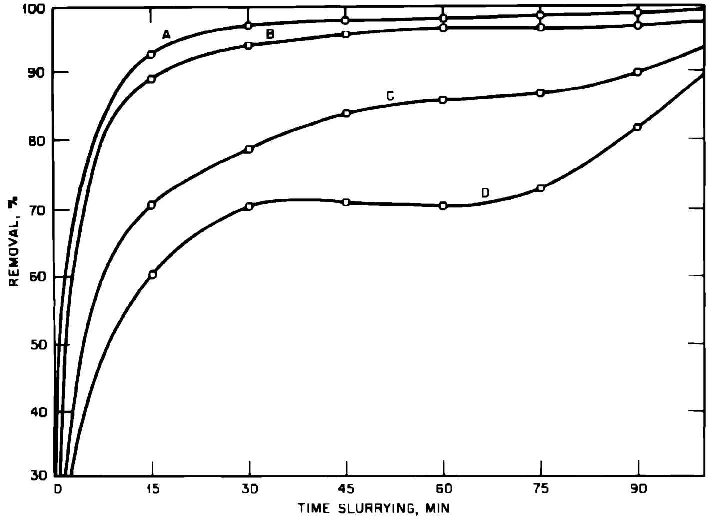

Fig. 2 Effect of increased contact time and concentration of ion-exchange resin on the removal of fission-product mixture 2. *(A)* 2,700 mg/l; *(B)* 1,800 mg/l; *(C)* 900 mg/l; and *(D)* 450 mg/l.

over 99 per cent occurred with Ce^{144}, Zn^{65}, Y^{91}, Nb^{95}, and Zr^{95}. These studies also showed that pH and coagulant dosages materially affect the removal of Sr^{89} and Sb^{124}. Therefore, Sr^{89} was selected for further study. It was found that with a pH of 11.3 and a phosphate-to-calcium ratio greater than 2.2:1, high removals could be effected.

(2) *Metallic Dusts.* Laboratory studies with metallic dusts by Lacy[20] yielded results summarized in Table 13-11. With the exceptions of fission-

TABLE 13-10 Removal of Radionuclides by Phosphate Coagulation

Nuclide	Coagulant	Coagulant dose, mg/l	Removal, %
Ce^{144}	KH_2PO_4	200	99.8
	Na_3PO_4	120	99.9
Sr^{89}	KH_2PO_4	100	81.3
	Na_3PO_4	240	97.8
Y^{91}	KH_2PO_4	100	99.9
Sb^{124}	KH_2PO_4	100	66.1
	Na_3PO_4	120	67.4
Zn^{65}	KH_2PO_4	50	99.6
W^{185}	KH_2PO_4	200	10.7
Zr^{95}	KH_2PO_4	100	99.5
Nb^{95}	KH_2PO_4	100	99.2

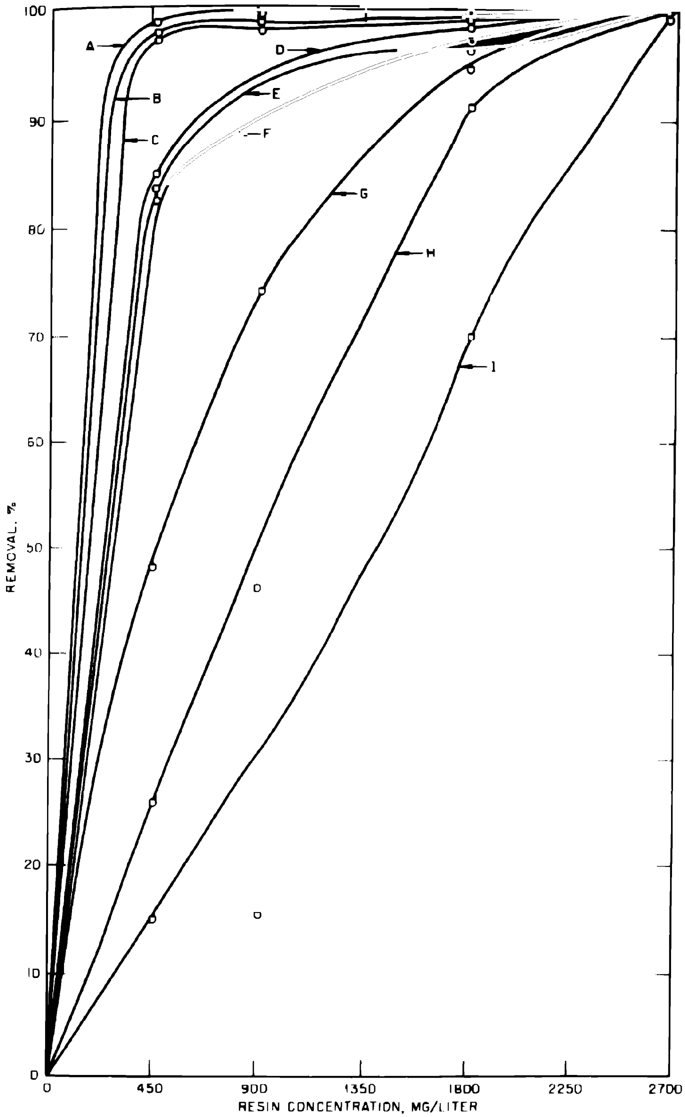

Fig. 3 Decontamination of radioactivity contaminated water by slurrying with ion-exchange resin MB-3 (90-min contact time). *(A)* Ta^{182}; *(B)* Ce^{144}-Pr^{144}; *(C)* $Zr^{95}Nb^{95}$; *(D)* Ba^{140}-La^{140}; *(E)* I^{131}; *(F)* fission-product mixture 2; *(G)* p^{32}; *(H)* Cd^{155}; and *(I)* Cs^{137}-Ba^{137m}.

TABLE 13-11 Removal of Radioactive Contaminants by Metallic Dusts (Metal dust, 1,000 mg/l, 90-min contact time, filtered sample counted)

Contaminant	Stock solution pH	Initial activity, counts/min-ml	Removal, %			
			Iron[1]	Zinc	Copper	Aluminum
Ru^{106}-Rh^{106}	8.0–8.2	1,975–3,950	99.6	98.4	93.7	92.8
Y^{91}	7.9–8.0	1,610–3,230	98.0	98.0		
Zr^{95}-Nb^{95}	7.2–8.3	1,210–4,470	99.1	97.9	99.1	99.8
P^{32}	7.8–8.4	128–12,000	99.8	98.1		84.2
I^{131}	6.5–8.2	4,288–6,689	37.2	45.7	42.2	23.2
$Ce^{141,144}$-Pr^{144} ...	7.9–8.1	3,915–4,491	99.9	99.9	99.5	99.8
Ba^{140}	7.9–8.2	4,644–10,205	94.8	74.5	65.7	73.8
Co^{60}	8.0–8.2	1,571–4,792	92.2[2,3]	....	47.8	30.2[2]
Cs^{137}-Ba^{137m}	8.0	13,085	8.6			
FPM-5[4]	2.0–7.2	2,890–4,220	55.5	39.6	49.3	8.2
FPM-6[5]	7.2–8.0	4,730–10,375	85.8	76.6	92.1	89.4

[1] Iron samples were centrifuged before counting.

[2] Metal dust, 500 mg/l.

[3] Sixty-minute contact.

[4] FPM-5, mixed fission-product waste containing mainly Cs^{137}-Ba^{137m} and Ru^{106}-Rh^{106}.

[5] FPM-6, iodine dissolver solution aged 20 days.

product mixtures, iodine, and cesium, removals with iron under the conditions reported were in excess of 90 per cent for the radionuclides studied.

(3) *Clay Treatment.* The effect of small amounts of clay (up to 100 mg/l) on the removal of radionuclides by coagulation and sedimentation was reported previously (Table 13-4). Additional results with greater amounts of clay are summarized in Table 13-12.[11,21–23] Although the addition of clay materially improved the removal of radioactivity, large volumes of clay and contaminated sludge must be handled.

TABLE 13-12 Effect of Added Clay on Removal of Radionuclides*

Radionuclide	Removal, %		
	100 mg/l	750 mg/l	5,000 mg/l
Ba^{140}-La^{140}	41	58	85
Cd^{115}	3	30	64
Ce^{144}-Pr^{144}	70–80	86	99+
Cs^{137}-Ba^{137m}	38	87	98.0
Sc^{46}	53	91.7	96.9
Sr^{89}	2-12	14-22	49–52
W^{185}	0	4	49
Y^{91}	22–45	56-70	93.6
Zr^{95}-Nb^{95}	93.5	99.0	98.0
P^{32}	.....	.....	78–82
I^{131}	.....	.....	9-20
Co^{60}	.....	.....	85-99+

*Local clay added to produce turbidity.

Removal of Nuclear Test Debris (Fallout) from Water

The removal of fission products from a natural environment poses problems that are quite different from those encountered in the removal of reactor-produced or reactor-separated radionuclides from laboratory solutions. The debris from a nuclear detonation contains radioactivity in soluble form as well as in association with particulate matter. Fallout is returned to the ground primarily with rainfall and some reaches streams during runoff. The easy-to-remove radionuclides are taken out by adsorption or ion exchange on soils, by deposition on vegetation and soil surfaces, and by filtration of particulate matter, whereas the hard-to-remove materials are carried with runoff to the streams. Limited data are available, but it must be remembered that removals are a function of the radionuclides that are actually present. Removal efficiencies[24,25] for four full-scale water-filtration plants (Cambridge and Lawrence, Massachusetts, and Rochester and Albany, New York) are shown in Table 13-13 and vary from 0 to 75 per cent.

(1) *Filter Backwash-water Activity.* The activity levels in slow-sand

TABLE 13–13 Removal of Gross Activity by Water-treatment Plants

Plant	No. of tests during period indicated	Date of sampling	Removals, %			
			Coagulation and settling	Filtration	Overall treatment	Overall tap water
Cambridge, Mass.	3	Apr. 8 to July 3, 1953	20.5–37.2	13.5–23.3	33.9–51.8	23.7–84.0
Lawrence, Mass.	4	Nov. 6, 1951 to June 30, 1953	16.4–56.2	0–67.4	12.7–75.0	40.4–80.8
Rochester, N.Y.	11	Mar. 16, 1951 to June 12, 1953	....	0–62.3*	0–64.8	0–66.1
Albany, N.Y.	...	May 18 to July 13, 1953	23.5†	6.8	28.7	

*Slow-sand filter results.

†Includes aeration.

filter backwash water (Rochester, New York)[24] are summarized in Table 13-14. Backwash-water activity levels varied, but in all cases the activity levels were approximately five or more times greater than those in raw water. If high raw-water activities are encountered, it may be necessary to consider the safe disposal of contaminated washwaters and the release of activity from the backwash water.

TABLE 13-14 Rochester, N.Y., Slow-sand-filter Backwash Activity Levels

Period	Number of samples*	Activity, counts/min-l		Concentration factor†
		Raw water	Backwash water	
Mar. 16–Oct. 31, 1951	39,37	0.70	3.75	5.35
Nov. 1–Nov. 15, 1951	12,12	12.3	205	16.6
Nov. 16, 1951–Jan. 1, 1952	31,30	0.89	22.1	24.7
Jan. 2–June 3, 1952	81,81	0.44	3.20	7.28
June 4–June 20, 1952	15,14	3.72	48.8	13.1
June 21–July 20, 1952	7,7	1.29	13.6	10.6
July 21–Nov. 1, 1952	29,29	0.352	2.40	6.82
Nov. 2, 1952–Feb. 1, 1953 ..	26,26	0.26	2.25	8.70
Feb. 3–Mar. 20, 1953	14,14	0.54	2.60	4.82
Jan. 2–May 12, 1953	37,37	0.398	2.53	6.35
May 15–June 12, 1953	8,9	0.53	7.62	14.4

*Number of tests of raw water and backwash water, respectively.

†Concentration factor = backwash-water activity/raw-water activity.

(2) *Sludge Activity.* Where chemical treatment is employed, activity associated with settled or precipitated sludge is accumulated, and thus considerable care must be exercised in the disposal of this contaminated sludge. Sludge activity levels encountered in the Rochester, New York, water-treatment plant[24] are summarized in Table 13-15. Sludge concentration factors ranging from 25 to 114 times the raw-water activity levels are indicated.

GUIDES AND STANDARDS

Basic recommendations for maximum permissible concentrations of a large number of radionuclides in water have been promulgated by the International Commission on Radiological Protection (ICRP) and the National Committee on Radiation Protection (NCRP). These recommended values have been incorporated in the regulations of the U.S. Atomic Energy Commission (AEC):[26]

> . . . for protection of licensees, their employees, and the general public against radiation hazards arising out of possession or use of special nuclear, source, or by-product material under license issued by AEC. These regulations, among other things, prescribe limitations which govern . . . concentrations of radioactive material which may be discharged into air or water. . . .

TABLE 13-15 Sludge Activity Levels at the Rochester, N.Y., Water-treatment Plant

Period	Number of samples*	Activity, counts/min-l		Concentration factor†
		Raw water	Sludge	
Mar. 16-Oct. 31, 1951	39,37	0.70	31.5	45.0
Nov. 1-Nov. 15, 1951	12,11	12.3	1390	114
Nov. 16, 1951-Jan. 1, 1952	31,24	0.89	65.0	73.0
Jan. 2-June 3, 1952	81,58	0.44	24.2	55.0
June 4-June 20, 1952	15,11	3.72	387	104.0
June 21-July 20, 1952	7,6	1.29	63.8	49.5
July 21-Nov. 1, 1952	29,25	0.352	20.4	57.9
Nov. 2, 1952-Feb. 1, 1953	26,23	0.26	22.0	85.0
Feb. 3-Mar. 20, 1953	14,14	0.54	21.2	39.2
Jan. 2-May 12, 1953	37,36	0.398	10.2	25.6
May 15-June 12, 1953	8,8	0.53	40.1	75.6

*Number of tests of raw water and sludge, respectively.

†Concentration factor = sludge activity/raw-water activity.

The values given in Appendix B, Title 10, Part 20, Code of Federal Regulations[26] are the concentrations to which licensees may expose persons in restricted areas or which may be released by licensees into the environment without specific approval of the Commission.

The Federal Radiation Council, charged with providing a federal policy on human radiation exposure, is to ". . . advise the President with respect to radiation matters, directly or indirectly affecting health, including guidance for all federal agencies in the formulation of radiation standards and in the establishment and execution of programs of cooperation with states. . . ."[27]

Radiation protection guidance for intake of specific radionuclides (Ra^{226}, Sr^{89}, Sr^{90}, and I^{131}) is given and includes total intake of these radionuclides from air, water, and food.[28] Intake values are given in Table 13-16, where

TABLE 13-16 Radiation Protection Standards Recommended by the Federal Radiation Council

Nuclide	Intake levels, pCi/day		
	Range I*	Range II†	Range III‡
I^{131}	0-10	10-100	100-1,000
Ra^{226}	0-2	2-20	20-200
Sr^{90}	0-20	20-200	200-2,000
Sr^{89}	0-200	200-2.000	2.000-20.000

* Calculations based on source information. Surveillance adequate to confirm calculations.

†Surveillance adequate to demonstrate levels. Control at source to avoid excess exposure as levels increase to top of Range II. Intakes do not exceed the recommended Radiation Protection Guides (RPG).

‡Surveillance to check effect of control actions. Control designed to reduce levels to Range II or lower. Intakes in Range III will result in exposures exceeding RPG if continued for a sufficient period.

those shown for the top of Range II correspond to the respective Radiation Protection Guides (RPG).

More specific guidance on water may be found in the *Public Health Service Drinking Water Standards*[29] which list concentrations for Ra^{226}, Sr^{90}, and gross beta activity in water used on interstate carriers. These are given in Table 13-17.

TABLE 13-17 Radionuclide Levels Recommended in the Public Health Service Drinking Water Standards

Radionuclide	Concentration, pCi/l
Ra^{226}	3
Sr^{90}	10
Gross beta activity*	1,000

*Sr^{90} and alpha emitters absent.

Few data on radionuclide levels exist on finished water supplies which permit comparison with the values recommended in the *Drinking Water Standards*. However, considerable data are available on gross activity and strontium 90 levels in surface waters of the United States.[30] These data are summarized in Figs. 4 and 5. Those in Fig. 4, for the period October, 1958, through early 1964, show that the median gross beta activity levels ranged from 0 to 90, the 90-percentile values from 45 to 383, and the maximum values from 176 to 7,343 pCi/l during a given month of sampling. Similarly, quarterly geometric mean values for Sr^{90} (Fig. 5) ranged from 0.51 to 3.2 and maximum values from 1.0 to 12.6 pCi/l. During the period of observation, it will be seen that the gross beta level of 1,000 pCi/l was exceeded 40 times, and the Sr^{90} level was exceeded during two quarters.

Because of the lack of direct information on activity levels in finished waters, the data for surface waters may be utilized in attempting to assess radioactive intake from water. As has been indicated earlier, water-treatment processes are effective for the removal of radioactive materials associated with turbidity (suspended solids) but not as effective when the radioactive materials are in solution. Of the 40 values exceeding the 1,000 pCi/l of gross activity, 20 showed high concentrations in radionuclide levels associated with the suspended solids fraction of the water, and all of these would be reduced to acceptable levels following primary treatment. Eighteen of the remaining 20 values are for the Columbia River at Pasco, Washington, which show high radionuclide levels associated with the dissolved solids fractions of the water. The degree of removal attained would depend on the treatment extant at Pasco and the efficiency for removing the various radionuclides discharged at Hanford. The remaining two values are from the Clinch River at Kingston, Tennessee, below Oak Ridge National Laboratory, and here again, the removal would depend on treatment facilities available and the radionuclides present in the water. Thus, it is

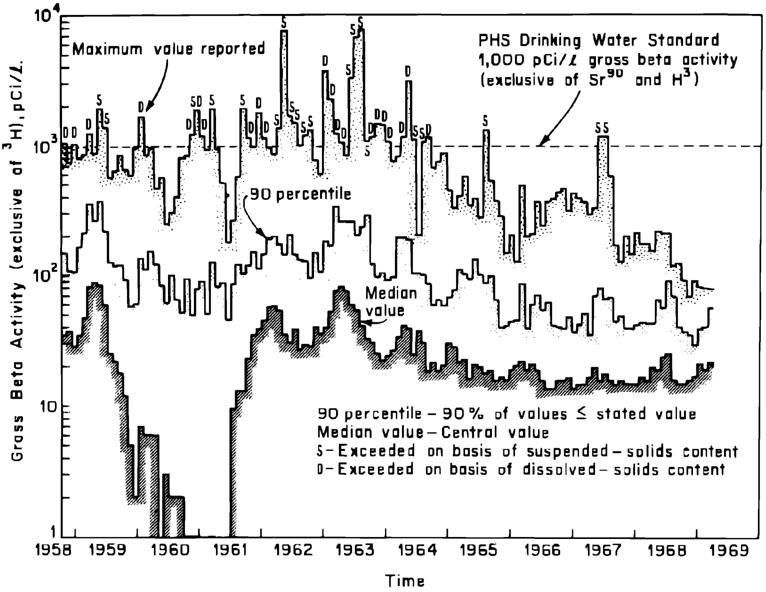

Fig. 4 Gross beta activity in surface water of the United States. National Water Quality Network values. Lower curve shows median concentrations, middle curve the 90 percentile level (i.e., 90% of values had a concentration lower than that shown), and upper curve shows maximum gross beta values reported during month.

seen that, except for the possibility of higher intake of gross radioactivity and of strontium 90 for short periods of time, water supplies do not contribute greatly to the overall exposure of population groups. Unpublished data[31] show less than 20 per cent of the total Sr^{90} taken into the body is ingested with water.

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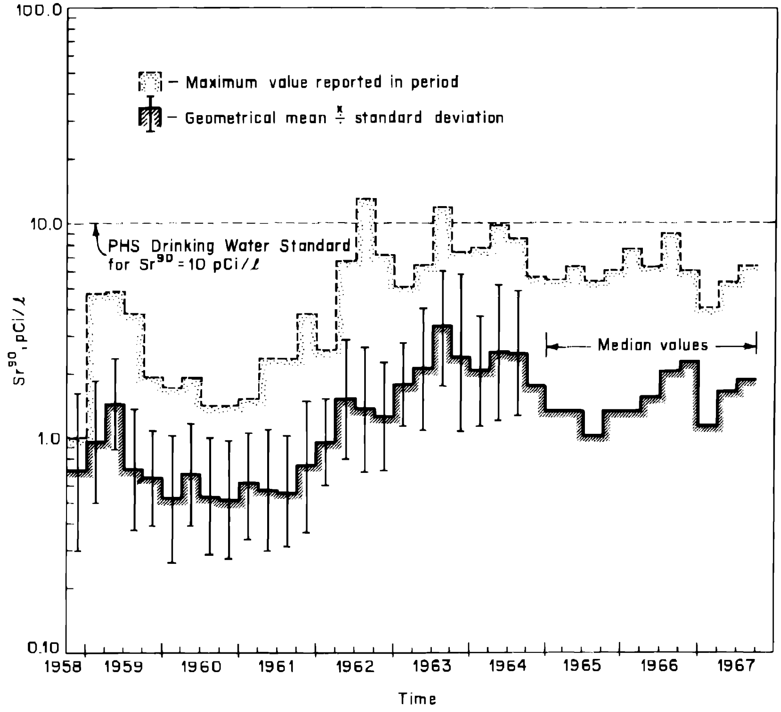

Fig. 5 Strontium 90 in surface waters of the United States, National Water Quality Network values. Lower curve shows $M_g \div \sigma$ (geometric mean and standard deviation) strontium levels; upper curve shows maximum values reported during period. The USPHS Drinking Water Standard for strontium 90 (10 pCi/l)is also indicated.

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14

Treatment-Plant Control

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The function of a water-treatment plant that serves the public is to continuously produce an adequate water supply that protects and promotes the health and well-being of individuals and the community. Such water may be described as wholesome and palatable and is of such importance that the task should only be entrusted to operators who have good qualities of character and judgment and have sufficient formal education to accept, understand, and apply fundamental training in hydraulics, bacteriology, biology, and chemistry. A wholesome water is uncontaminated (unable to infect or poison the user) and free from excessive amounts of mineral and organic matter. A palatable and aesthetically acceptable drinking water is free, or practically free, of color, turbidity, taste, and odor and is of moderate temperature.

Few raw water sources can, without treatment, supply water with these attributes. Groundwater from wells, for example, usually requires disinfection for complete public health protection. Other groundwater sources may need additional treatment for the control of staining and discoloration to reduce hardness and excess fluorides, and in some instances to increase the pH of the water to prevent corrosion. Entrained gases, such as methane and hydrogen sulfide may also need to be removed from some groundwater supplies before distribution to prevent explosion and fire hazards as well as foul odors and a poisonous gas from reaching the customers.

Surface water sources (from streams, lakes, or impoundments) should never be used by the public without treatment. Besides pathogenic bacteria and viruses, turbidity, color, biologic forms, and domestic and industry wastes (if present) must be removed or destroyed to prepare the water for public use.

Even with the simplest types of treatment and in the smallest plants, the public's dependence upon water treatment is such a serious responsibility that only qualified personnel should have responsible charge of the product of a plant. As the degree of complexity of water treatment increases, the expertise and skill required to produce a high-quality water also increases.

Water treatment may range from simple to highly complex operations handling small or large volumes of product. Most treatment operations require constant supervision. Although advancements in the knowledge and technique of treatment processes are constantly being made, it is not yet prudent to remove the human element from these operations entirely. Automation is being increasingly employed in plant operations and may be expected to take over many tedious jobs in the future. However, under no circumstances can automation make final judgments on safety and quality of product. Such judgments must be the prerogative of highly skilled operators. Today, quite a few states, through their health departments, certify by examination the qualifications of operators of water-treatment plants serving the public. Usually several categories of operator certificates are available, covering a range of from minor to major water-treatment processes. In the states having mandatory operator-certification programs (provided by law) only qualified personnel are employed. Some other states have voluntary certification programs (usually promoted by the local association of waterworks people) under which the percentage of eligible operators that are certified is usually low and leaves much to be desired. States having voluntary programs should seek the mandatory type, as should the states presently having no certification programs. Both types of programs provide improved plant operation and product and enhance the professional status of the certified operators.

Water-treatment plant control comprises the constant operation and management of facilities and personnel. Consideration must be given to such factors as competent personnel, standards of water quality, plant maintenance and cleanliness, analytical laboratory control, measurements of water flow, chemical application control, operation and maintenance of chemical feeders and other plant equipment, storage and quality of chemicals, plant records, and safety.

PERSONNEL

As previously pointed out, the operation of water-treatment plants, both small and large, must rest in the hands of qualified persons. The number of such employees in a plant depends principally upon its size and to some extent upon the quality of the raw water and the type of the treatment processes used. For the larger plants qualified operators should be present on every shift. At the smaller plants one qualified operator is usually responsible for the total operations, with the nonqualified operators following his strict instructions.

For the larger plants the chief operator should have at least a Bachelor of Science degree (or equivalent) in sanitary engineering, chemical engineering, chemistry, or biology and a few years of experience in plant operation. In addition the chief operator should be a good manager and be familiar with hydraulic principles as applied to waterworks operation; know and recognize public health hazards inherent in water supply, treatment, and distribution; be acquainted with waterworks safety practice; be familiar with the chemical, bacteriological, viral, and biological conditions that occur in water treatment; be able to perform chemical, radiological, bacteriological, and biological tests and make proper interpretations of the test results to assure proper plant operation. He should have an intimate knowledge of the drinking-water standards of the state department of health and of the U.S. Public Health Service and should be able to operate plant equipment and supervise plant personnel to continually attain these goals.

In addition to a technically qualified chief operator (or manager) the water plant should also be staffed with an adequate number of competent (preferably state-certified) operators and maintenance men. Thus the staff would be highly qualified to handle operations in any eventuality such as vacations, illness, or in an emergency situation.

At present there are no national requirements for the number and type of qualified operators needed in the various kinds of treatment plants, although states with mandatory certification are definite in this area. A small water-filtration plant (up to 10 mgd) operating 24 hr a day and treating a surface supply might well require the following nine-man operating staff:

1 plant superintendent and chief operator
4 plant operators (one per shift, three shifts per day, four 42-hr work weeks)
1 maintenance mechanic
3 general utility help (Duties would include chemical handling, grounds care, operators' vacation and holiday relief, mechanics helper and basin cleaning)

A larger plant (10 to 20 mgd) may require an additional operator at each of the following stations: (1) the filter building, (2) the chemical feed room,

(3) the low-lift pumping station, and (4) the high-service pumping station. The maintenance staff would be proportional in size to the amount of equipment and grounds under its care. In treatment plants of large size (20 to 50 mgd), pumping operations sometimes becomes a separate department. However, in a plant as envisioned above, on a three-shift, 42-hr week basis, a treatment and pumping plant might reasonably require a minimum staff of 40, as follows:

1 plant superintendent*
1 assistant plant superintendent*
3 chemists and bacteriologists*
4 chemical building operators
4 high-service electric pumping station operators
1 stenographer
4 low-service pumping station operators
4 filter plant operators
2 basin men
5 maintenance mechanics
10 general utility helpers
1 supplies and store keeper

NOTE: Asterisk denotes employees that should be highly qualified (certified where required) in their duties.

In even larger plants (over 50 mgd) a further division of duties may be made. For example, some of the country's largest systems have a separate quality control and research section, leaving routine operations to control chemists and technicians. Local conditions and demands play a role in the type and size of the operating organization that is adopted.

A water utility disinfecting a groundwater supply with chlorine would obviously require a relatively small operating staff when compared with the staff required for a water-filtration plant processing an equal amount of surface water. The addition of chemical treatment for corrosion control (to disinfection) will probably not require additional operating personnel.

However, when treatment of such a groundwater source for iron and manganese removal or defluoridation is required nearly as many operators will be needed as for a plant of comparable size treating surface waters.

Whatever the size of the staff, the selection of water-treatment personnel should be made on the basis of education, experience, dependability, and integrity. In determining competence and educational qualifications for any specific position, consideration must be given to local civil service and state department of health certification requirements. Careful selection should also be exercised in hiring employees for lesser plant positions, since these men through in-plant study and training should have the ability to advance beyond the jobs they are being hired to fill. Internal advancements are also good for employee morale, staff stability, and individual incentive.

Each member of the staff should be carefully indoctrinated with the relationship of his duties to the health and welfare of the community for which he works and should be shown that negligence on his part could be responsible for a serious public health emergency, such as a waterborne epidemic. As "professionals" all water-plant operators should keep up with water-treatment trends and developments by attending state and national conferences on water-supply subjects as well as becoming active members of the American Water Works Association. The association's "Code of Practice" should become the operator's professional work guide.

Where experienced operators are not locally available to start and control the operation of a new water-treatment plant, it is essential that a qualified chief operator be employed from outside the community. He should be employed several months before the plant is placed in operation to permit him to select and train local people for the routine jobs of operation. The newly employed people should be encouraged to attend operator training courses locally available in almost every state. These courses are sponsored by the state departments of health, universities, and state and national technical associations.

Delegation of Responsibility

A well-defined policy for the delegation of responsibility among plant personnel for all phases of plant operation is vital and must be resolved by management before the problems of personnel can be judged to be under control.

The local water board and the utility manager must recognize that authority must not be assumed by any employee but must be delegated. Authority, commensurate with the responsibility involved in any position, is conferred solely by management upon the employee. Authority conferred must be written, concise, never overlapping, and should cover all phases of plant operation. This is true for all plants, regardless of size.

Authority, with its resulting responsibility, may often be vague or merely implied rather than clearly defined. Operational failures have resulted from misunderstanding of an employee's authority and duties. Plant inefficiencies and confusion are certain to develop if employees are not certain of their duties. This is why all duties should be in written form.

An excellent means of achieving proper delegation of authority is with a general organization chart, which shows the relationships between all supervisory employees of a utility, followed by more detailed charts outlining the specific duties and defining the relationships between all employees in the divisions. All employees should have access to these charts and should understand clearly the authority accompanying the various jobs. As duties change, the charts should be revised accordingly and due notice given to the employees affected.

The organization chart must be recognized as only a means to an end.

Once authority has been delegated, it must be recognized and respected by each member of the staff. Delegated authority must never be bypassed. Regular staff meetings of all supervisory personnel are an aid in obtaining the smooth, efficient operation and cooperation that are required.

QUALITY SPECIFICATIONS FOR FINISHED WATER

Each treatment plant should have a quality standard for its product. Plant control can become an indefinite and uncertain procedure unless production is geared to definite specifications of quality. The quality goals should be recognized by all plant personnel and a constant effort made to adhere to them. Unless the water flowing through a plant is scheduled to receive treatment to achieve a predetermined end, the plant cannot be considered to be under proper control. The quality of the finished water should be uniform.

Minimum drinking water standards for safe water are those of the U.S. Public Health Service established for common carriers. The state departments of health of the United States usually accept them, without change, for all drinking-water supplies within their boundaries. In January, 1968, the American Water Works Association adopted quality goals for potable water[1] to upgrade the consumer characteristics of water supplies and thus serve the public with a better product. The AWWA goals are voluntary in their application and relate largely to the aesthetic or consumer-oriented characteristics of a water supply such as clarity, taste and odor, softness, color, and corrosiveness. See Chap. 1, "Water Quality," for details. The Public Health Service *Drinking Water Standards*, in contrast, are mandatory where the public health is involved and voluntary or advisory in the nonhealth aspects of the standards.

TREATMENT-PLANT APPEARANCE

The general appearance and cleanliness of the treatment plant and grounds can greatly influence the attitude of the public toward a utility. A clean and well-maintained plant will suggest a safe and potable product and competent management in which the public may have justifiable pride.

One of the greatest assets a public utility can earn is consumer confidence and goodwill. Consumer confidence can actually promote public health, for a community without confidence in its water supply may resort to the use of water from questionable sources. Public goodwill toward the water utility and a justifiable pride in the treatment facilities and its product will materially help in securing rate changes for needed additions.

The importance of a clean and well-cared-for treatment plant cannot be overemphasized. In addition to the psychological influence of a clean plant on public opinion, it will also help the water-plant operator to understand that he is part of an industry in which cleanliness has an important bearing on the quality of the finished product.

ANALYTICAL LABORATORY CONTROL

Analyses and tests at filtration plants are made to control water treatment, to record plant performance, to improve plant performance, to undertake research and development of tasks of value to the plant and to the profession in general. Tests designed to control water treatment should present evidence that: (1) the water has been properly prepared for each major step in the treatment process; (2) each key process—such as mixing, coagulation, settling, filtration, softening, iron and manganese removal, disinfection, and taste and odor control—has proceeded according to plan; (3) the finished product is clear, free from taste and odor, free from undesirable chemical characteristics, and safe for human consumption. Special emphasis should be placed on tests that are of immediate value in the assessment of water quality and safety. The residual-chlorine and turbidity tests are in this category, but bacterial tests, because of the time required for completion, are not, although of great importance for other reasons. Consideration should be given to instrumentation of such early-value tests to provide continuous recording at strategic points in the treatment process.

Filter and plant-effluent turbidimeters and residual-chlorine and pH recorders are examples of equipment that have proved their value in plant operation. Pilot filters for optimum evaluation of the coagulant dose are now being developed for better plant control.

The number of water samples examined each day will depend upon the quality of the raw water, the rapidity with which raw water characteristics change, the multiplicity of processes used in the treatment, and the number of processing units involved. In general, the number of water samples examined at each stage of the total treatment should be adequate to provide positive control and assure the delivery of quality water to the public. All plants should collect water samples for chemical and bacteriological testing on an 8-hr shift basis or at least three samples a day. In addition, samples should be collected hourly, to check each key step in the treatment. Considering the minuteness of a water sample compared with the volume of water treated, it is doubtful if too many samples can be examined.

Because of the importance of what may be termed "primary control tests" (turbidity, color, residual chlorine, alkalinity), these should be made by the operators on each shift and minor corrections in treatment made as indicated in accordance with planned and approved procedures. Confirmation by the laboratory staff or plant chemist should follow. The primary control tests are simple and should be made frequently. They become the initial signals of changes in raw water characteristics and plant performance and therefore represent the first line of control in the treatment process. Frequent tests of the control type during all 24 hr of the day are the means by which safety and uniform quality of the product can be assured. Continuous, automatic monitoring, where possible, can provide even greater assurance.

Examination of water samples taken regularly from established sampling stations on the distribution system for bacteria, clarity, taste and odor, and chlorine residual is necessary to ascertain that the water is of high quality as it reaches the consumer. Water quality deterioration in the mains is possible and must be recognized and controlled. The frequency of sampling the water in the distribution system should conform closely with the recommendation made in the current Public Health Service *Drinking Water Standards.*[2] The minimum number of samples is empirically based upon the population served and is designed to give a reliable and useful picture of the quality of the water served the consumer. Various factors other than population may, of course, necessitate examination of more samples than is recommended.

The type of analysis made on water samples is dependent upon the point of collection, such as from the raw water, the plant processes, the plant effluent, or the distribution system. The methods of analysis should be those specified in *Standard Methods for the Examination of Water and Wastewater,*[3] prepared jointly by the APHA, AWWA, and WPCF and revised on a 5-year basis. Uniformity of methods of analysis among water laboratories is important because it permits comparison of results and enables management, health, and legal authorities to evaluate the finished water in reference to accepted public health and utility standards.

Almost all laboratories make routine tests for residual chlorine, turbidity, alkalinity, pH, color, and coliform bacteria. Many laboratories include routine tests for hardness, taste, odor, calcium, and total and dissolved solids. Plants using lake, stream, or impounded water may routinely make algae examinations. Plant treatment involving coagulation and sedimentation will require a program of testing designed to establish the efficiency of these processes. Experimental stirring units for laboratory rating of dosages of chemicals are in common use for this purpose.

Each key step in the treatment routine must be supported by laboratory tests that clearly demonstrate its effectiveness. To test the efficiency of filtration, for example, equipment should be provided for measuring turbidity accurately down to 0.1 j. u. or less. A cotton plug filter placed in each filter effluent line may also be desirable. When softening is practiced, the accurate determinations of calcium and magnesium are required. For iron and manganese removal or for taste and odor control, suitable tests must be made routinely, frequently, and with precision. Since public safety is a primary objective of every potable-water plant, adequate tests and records of bacteriological quality are most essential. The coliform test is universally used in this country to ascertain bacterial quality.

Each revision of the U.S. Public Health Service *Drinking Water Standards* is preceded by a thorough and critical review of recent research, practical water-plant experiences, and water-related epidemiology to assure that the previously recommended tests are adequate or if revisions are needed. These reviews to date have not resulted in changing from the coliform group of bacteria as the indicator of contamination. The Public Health Service *Drinking Water Standards*[2] state:

> The presence of any type of coliform organism in treated drinking water suggests either inadequate treatment or access of undesirable materials to the water after treatment. Although there are some differences between strain and subgroup organisms with regard to survival under natural conditions and resistance to chlorination, in general all the coliform organisms exhibit survival and resistance patterns in the same order of magnitude. The presence of coliform organisms in treated water calls for definitive action for their elimination.

The absence of the coliform group of organisms in the finished water is considered a reliable indicator of the adequacy of treatment and the absence of pathogenic bacteria. Whether these conditions can be extended to include rickettsial and viral organisms has not been definitely established. However, some evidence has tended to show that the coliform test is not without its limitations.

LABORATORY EQUIPMENT

Adequate laboratory control presupposes a well-equipped, properly staffed laboratory. The size of the laboratory depends upon the nature of the processes to be controlled and, to a lesser extent, upon the size of the water plant. In general, it is advisable to divide the laboratory into several areas used for specific purposes, such as bacterial, chemistry, microscopy, and preparation. All space should be well-lighted, clean, comfortable (air-conditioned), and used for laboratory purposes only. For small plants, the various laboratories may be consolidated into one room, with the various functions allocated to different sections of the room. In the larger plants an individual room houses each specific laboratory. In some cases, the plant control tests made by filter operators can best be made at a location removed from the main laboratory and closer to their work areas.

The laboratory equipment must be adequate to permit proper analytical control of the treatment process. Space does not permit an itemized list of equipment required for all laboratories. In general, such items as an incubator, sterilizer, drying oven, refrigerator, balance, turbidimeter, water still, pH meter or comparator, chlorine comparator or titrator, laboratory tables, reagents, cabinets, hot plates, and glassware are included.

Laboratory personnel must be educationally qualified and well trained in water-treatment-plant control. They should be certified by examination as to their qualifications by the state department of health. The person in charge of the laboratory should preferably be a chemist or bacteriologist, possessed of a background of experience in adequate laboratory control of water-treatment processes. In the smaller plants, at least the chief operator should be certified as to his qualifications. The filter operators should have the training in laboratory technique provided by state department of health waterworks short courses.

Measurements of Flow and Chemical Feed

Plant operation requires the accurate proportioning of the treatment chemicals to the water being processed, and proper proportioning is dependent upon accurate measurement of both water flow and chemical feed. These measurements of volume of water being treated and the weights of chemicals being fed should be within 2 per cent of accuracy either way.

Water that is being prepared for human consumption must be subjected to the same careful processing control that is required of the food industry, if the product is to be consistently uniform and satisfactory. Inaccurate feeding of chemicals could be hazardous to the health of the community, economically wasteful, and could cause public resentment with treatment resulting in obnoxious tastes, odors, high turbidity, or color in the water. For these reasons plant personnel must always be qualified professionally.

All rate-of-flow water measuring devices in a plant should be checked periodically. At least once each year the registration of these instruments should be compared with a time-volume displacement of water in a basin, clearwell, or storage tank. They may also be checked against the flow recorded by other meters that measure component parts of the flow. The periodic recalibration of the primary flow measuring device in a plant and the checking of the register may be necessary to determine the meter's accuracy and dependability. Only when a meter is periodically checked can the indicated flow be considered accurate.

Similarly, chemical feeders must be routinely checked for accuracy. To check dry feeders, it is desirable to catch the feed for a short period of time and to weigh the catch on scales. The overall accuracy of chemical feed should also be checked by a comparison with the storage record, that is, by checking the indicated amount of material used against the amount actually in storage at the end of the month. Sometimes, too, the accuracy of chemical feed can be established from the chemical analyses of the water being treated. Performance of solution tanks, slakers, and similar equipment should also be checked periodically by comparisons of the actual changes produced in the water treated with the theoretical changes that should have been effected by the quantity of chemical fed. Every plant should develop a testing routine for its flow-recording and chemical-feed equipment.

Control of Basin Operations

Purification plant basins require routine care and operational control. To prevent impairment of the quality of the water, organic matter, animal life, and debris must be either kept out of the basins used in treatment or quickly removed from them. The covers, vents, and screens on finished-water basins must be routinely checked for defects. Sedimentation basins must be periodically gaged for sludge accumulation and any sludge must be removed from them before the operating efficiency is degraded or before tastes and odors are imparted to the water. In basins equipped for mechanical sludge removal, the operation of these devices must be checked from time to time to ensure proper functioning.

In the winter, it is important to prevent short circuiting of the flow in the basins due to ice formation. In some plants, ice coverage of the entire basin surface is prevented to protect the basin walls. The establishment and growth of algae in basins must be controlled by regular inspections and treatment: otherwise troublesome tastes and odors, clogged filters, and unsightly conditions may develop. Also, drainage of surface water into basins should be avoided because it may affect the taste and sanitary quality of the water.

Filter Operation

Ineffective filtration may be caused by dislocations in the gravel bed, dirty filter sand, and malfunctioning of filter-rate controllers. Regular monthly probing of the entire filter area to establish the upper surface of the gravel bed will reveal if gravel mounds exist through which water can pass at higher-than-desirable rates. Inspection for mud balls and shrinkage of filter sand away from the filter walls will indicate if improper washing and cleansing of the filter media exists. Also, rate controllers may cease functioning properly and allow excessive filtration rates through the filter. Loss-of-head devices and rate-of-flow controllers require periodic checking to function well. The washwater rate and length of filter washing period should be set by the chief operator rather than left to the filter operator's judgment. Changes in filter-operating instructions should be made relatively frequently as water temperature and other conditions dictate.

Planned Plant Maintenance

Proper plant operation should include a regular inspection and maintenance program that will serve to eliminate equipment breakdowns and thus permit the continuous functioning of the plant. Such a plan is known as "preventive maintenance." This entails regular inspections and lubrication of equipment and the prompt restoration or repair of worn parts.

To prevent breakdowns, all mechanical equipment should be periodically disassembled, systematically inspected, lubricated, and overhauled. To do this requires the keeping of a system of permanent records on every operating piece of equipment. It is unwise to depend upon memory or the personal notes of supervisors for the scheduling of preventive maintenance. To do so is comparable to allowing the knowledge of distribution-system piping and valve locations to exist only in the memory of an employee. A planned maintenance program should be designed to accomplish the following objectives:

1. Schedule inspections, lubrication, and necessary repairs of regular and standby equipment on a definite periodic basis.
2. Time preventive maintenance work so that it is evenly distributed throughout the year.
3. Systemize scheduled maintenance work so that it is referred properly and without fail to the maintenance department or crew.
4. Provide a simple procedure for changing the frequency of inspections of any or all items as required.
5. Create a dated record, easily and quickly accessible, of the maintenance work required and performed upon each item of equipment.
6. Standardize each inspection procedure, itemizing and illustrating all items to be covered.
7. Schedule maintenance work so that similar or related work is done consecutively.
8. Provide a readily accessible record of the maintenance work to be performed upon each piece of equipment at given times during the year.
9. Create a means of determining the cost per year for maintaining any item of equipment.

RECORDS

Records are used for review purposes, for providing the basis for improvements and changes in operations, for future planning, for evidence, for financial purposes, and for securing economical results. As the use of computers increases it can be expected that records of water quality will become even more useful. Any laboratory that serves an agency having a data-processing section with the usual electronic equipment can greatly facilitate the handling and maintenance of laboratory records.[4]

Treatment-plant records usually begin with tabulation of the results of daily tests made on separate operations at various times during the day. These records may cover, for example, pump operation, chemical-treatment details, filter operation, laboratory water quality data, confirmatory tests, and distribution system quality and operation data. Some of the data will be recorded from gages, from tests, and from charts on which a summary of results is usually placed on the back of the record.

To make this mass of data usable, it is usually summarized and placed on a larger monthly-by-days record sheet, approximately 24 in. wide and 36 in. long. This becomes a permanent record and is usually kept on a current-year basis between hard covers for easy access and comparison. Almost every plant uses different kinds of record forms, but the larger sheet mentioned will generally be found to be uniform within each state since the state departments of health usually provide them. Forms and records have a way of perpetuating themselves, and for this reason the necessity for even the most important record should be studied regularly to make certain that the data being collected remain used and useful. Obviously, as few report forms as feasible should be used and kept in permanent files.

Standard Operating Practice Manual

Plant personnel should be trained continuously. Only when the entire staff is constantly improving its knowledge and skill in plant operations can treatment control be considered to be established on a sound basis. Like all knowledge and skills, those of water-treatment-plant operators can never be static, since there is a tendency toward stagnation or even regression when they do not progress. Thus, good plant operation requires some type of continuous personnel training. In larger plants, a class or conference room properly equipped with visual aids is of great assistance for an in-plant training course.

A valuable tool of any such training program will be a constantly expanding manual of treatment practices and methods of operation. By referring to such a manual and by helping to improve and enlarge it, an operator will keep alert to progress in the field and benefit from the experience of his fellow employees. Its availability to new employees can also materially shorten the preliminary training or breaking in period.

The standard practice manual can best be assembled as a loose-leaf compilation of operating instructions for all equipment and appurtenances. Recommendations and explanations of design and function of various parts of the plant by the consulting engineer could well be included. Such a manual should be indexed by the processes, facilities, and equipment for which it was prepared.

SAFETY PROGRAM

Since its trained personnel is the plant's most important asset, an important phase of plant operation is the protection of personnel through an active safety program. Passive agreement with safety regulations and practices will not prevent accidents and their serious interference with plant operations. Employee safety meetings, safety posters, distribution of abstracts of articles on safe practices, membership in national safety organizations, and similar techniques may properly be made a part of a program designed to make every employee safety-conscious.

Safety practices and regulations that should be made a part of the safety program include:

1. Dissemination of knowledge about the hazards and safety handling of waterworks chemicals. The Chlorine Institute,[5] the American Water Works Association, and suppliers of the various chemicals should be contacted for information and safe-handling instructions.
2. Enforcement of rules and education in the proper use of goggles, respirators, and gas masks.
3. Consideration of the possibility and causes of electrical accidents within the plant.
4. Proper use of tools and power equipment.
5. Safe use of ladders.
6. Artificial respiration technique.

It may be necessary to conduct frequent and intensive educational campaigns to teach even the most reliable of workmen that the use of safety equipment is not a sign of weakness and that it need not mean discomfort. It is important also, that the protective equipment used by the men be adequate to protect against the potential hazards to be encountered. Insurance companies can often provide experienced lecturers on plant safety programs.

RESEARCH, DEVELOPMENT, AND PLANNING

Research and development must be the means by which any industry develops and provides a better product and service to its customers. Thus all treatment-plant personnel should take an active part in the local system's planning program. Listed below are a few general ideas in which a water-treatment-plant operator might get interested to help solve some local problems. Many other questions of smaller magnitude would doubtless come to the minds of the conscientious and curious operators who may wish to find ways to do a better job. For example, the rainfall, runoff, and water quality records of suggested future sources of supply can provide an interesting study, but be certain that the records cover 10 or more years. New developments that promise to increase capacity of treatment units need to be carefully evaluated on the basis of local conditions. Similarly, studies need to be made of methods and facilities that will assure plant-effluent quality in the distribution system and its economical production. Such investigations may not produce world-shaking results and may even be of negative value, but nonetheless an investigation shows recognition of a problem, which may develop a new approach to the subject.

WATERWORKS LITERATURE

Proper plant control depends also upon the use of the best methods available. The plant office or laboratory should be provided with facilities for housing a library of handbooks, waterworks periodicals, and association journals. A good list of standard texts and handbooks will be found in the current *American Water Works Association Yearbook.*[6] Additional valuable information on water purification is contained in the journals of professional societies, in municipal reports, in trade journals, and in general waterworks magazines. These should all be available to the waterworks operator so that he may keep himself informed of new developments and changes in the art and practice of water purification.

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Quality Control in Distribution Systems

By H. J. ONGERTH

Control of water quality in the distribution system seeks to preserve the basic characteristics of water during its conveyance from the point of production and treatment to the consumer's tap. Often it is taken for granted that a clean, palatable water entering the distribution system will be just as good at the point of delivery to the consumer. To deliver a completely satisfactory water to the consumer, quality control must be provided. Theoretical conditions for attainment of complete control are: (1) the finished water is completely stable in its compositional and physical attributes; (2) it is biologically sterile; (3) the conveyance system and accessory structures are reactively inert to the water being conveyed; (4) the conveyance system is sealed off from contaminating intrusion. These conditions do not completely exist in the operational distribution system.

The Public Health Service *Drinking Water Standards* have long formally recognized the necessity for protecting water quality in distribution systems. The 1925 standards, in part, stated, "The water supply system including . . . pipelines, distributing reservoirs, mains and service pipes, shall be free from sanitary defects." The next (1942) edition of the standards gave direct attention to this subject, and the preface to the edition states:

> The results of recent studies on the potential pollutional hazards existing in the water supply systems of our communities due to faulty plumbing practices, cross-connections, interconnections, etc., as well as the pollutional hazards which are due to faulty water plant and distribution system operational practices, any or all of which may jeopardize the safety of the water in the distribution system, have been adjudged as being of prime importance in the consideration of the requirements of these Standards.

In recognition of these safety aspects of water quality, the 1942 standards required (for the first time) that, "The biological examination of water . . . shall be of samples collected at representative points throughout the distribution system." Further, as to source and protection, the standards expressly stated that, "Responsibility for conditions in the water supply systems shall be considered to be held by the water purveyor from the source of supply to the connection to the consumer's service piping." The current (1962) standards continue these requirements.

The pertinent major water quality factors are safety, taste and odor, appearance, and chemical balance. Water quality may deteriorate because of poor-quality water put into the distribution system, chemical interaction between water and pipe, biological degradation, biological infestation, cross connections, inadequate main disinfection, defects in storage facilities, and other less common factors such as blowoffs and vacuum or air relief valves improperly constructed or located. The consequences may be one or more of the following: unsafe water, turbid or rusty water, unpleasant taste and odor, or colored water.

SAFETY

Water treatment does not usually produce coliform-free water. The control of coliform organisms is relative, not absolute. Further, no distribution system will be free from coliform organisms unless residual chlorine is always present and other adverse conditions do not exist. Since these organisms are *indicators* of pollution and in waterworks practice are considered not to be pathogenic, their presence in water supplies may or may not have public health significance. In other words, they may have originated from benign sources. However, to be safe, coliform bacteria should always be considered *presumptive* evidence of pollution until proven otherwise. Hazardous sources of coliforms include cross connections, ineffective or nonexistent main disinfection, and infiltration during periods of low or negative pressure. Objectionable but usually nonhazardous sources of coliform include unprotected distribution storage (for example, from wind-blown dusts) and joint-packing infections. A major nonhazardous source of coliform bacteria in distribution systems is reproduction within the system—sometimes referred to as "aftergrowths." Each of these will be discussed.

Cross-connection Control

A cross connection is a hydraulic linkage permanently or temporarily connecting a source of pollution with the pipes of a potable water supply. Cross-connection hazards may range through a spectrum of high to low order. The principle has generally been recognized that the degree of protection should be appropriate to the degree of hazard. Further, the degree of protection is a combination of the type of device provided and the extent of testing and maintenance of that device. Backflow protection may be provided by air-gap separation or by installation of such devices as a double-check valve assembly or a reduced-pressure-principle backflow preventer. Cross connections may result from either "pumping" or "backsiphonage" hazards.

Pumping hazards, as used herein, are defined as those potentially causing backflow of foreign liquids into the community water system, resulting from interconnection of the domestic water system to a second system of pipes, tanks, or the like, containing water or other liquids under pressure maintained from some source other than the domestic water system, which pressure may be, or can be, higher than the pressure in the domestic system at the point of interconnection. Pumping hazards can exist at water-service connection to sewage or storm water pumping stations, sewage-treatment plants, waterfront property, industrial plants handling liquids under pressure, and buildings where sewage is pumped on the premises. Such interconnections may result in large quantities of dangerous materials entering the domestic water system.

Pumping hazards which may permit backflow of sewage or toxic chemicals into the public supply are highly dangerous. A high-order hazard also exists on premises where an auxiliary water system is maintained whose source is a polluted stream, bay, or lake and for which no treatment or inadequate treatment and control is provided. Further, all auxiliary water sources not under public health surveillance must be regarded with suspicion, though some auxiliary well sources may produce safe water.

A top-priority item in a cross-connection control program is to protect against these pumping hazards in a system. Such protection may be obtained by removal of the basic cause (such as abandonment of a sewage-polluted auxiliary source), by delivering water from the community water supply overhead—through an "air-gap"—to a receiving tank or by installation of a backflow-prevention device at the service connection. The latter two actions will protect the community water supply but will not protect the people drinking water within the the property under discussion.

Some health authorities will accept only air-gap separation (or abandonment of the polluted auxiliary source) as protection against the above-stated pumping hazards. Where an air-gap separation is not practical, some health authorities will accept a reduced-pressure-principle device.

Many industrial premises handle nontoxic materials under pressure, for example, carbonated beverages. Cross connections permitting backflow of such materials into the community water supply may not create public health hazards but can create objectionable conditions. For nontoxic materials a program to eliminate internal (on the customers' premises) interconnections, or in the absence of assurance of freedom from such interconnections, installation of an approved double-check valve assembly at the service connection, can provide acceptable protection.

Another means of contaminating the community water supply is through backsiphonage. Backsiphonage can occur when negative pressure develops, either in the water user's piping system or in the community piping system.

"Negative" or subatmospheric pressures in a piping system can result in transferring polluted or used water or other liquids from water-using fixtures into a building piping system and, under extreme conditions, even into the community water system. Backsiphonage hazards therefore generally present a relatively low-order threat to the community water system, but may present a high-order hazard to water consumers within a building or industrial plant. Negative pressures more frequently occur in building piping systems, due either to insufficient internal hydraulic capacity or to low pressure in the community water system. Negative pressures also occur in community piping systems—due to main breaks, planned shutdowns, fire demands, water usage exceeding the hydraulic capacity of the system, and other reasons.

As long as pressure is always maintained at the point of service from a community water system to a customer's piping, backsiphonage will not affect the community water supply. However, longer-than-instantaneous periods of negative pressure in the community water system can result in backsiphonage of water from a customer's piping system into the community system. If plumbing defects exist in this customer's piping system, then such siphoned water may be contaminated and, in turn, may contaminate a portion of the community water supply.

Negative pressure in any part of a community water system should never be tolerated. This stipulation is necessary to prevent picking up contamination from sewers in the street or from inadequate plumbing. To always know what is going on within the system, good management relies on one or more water-pressure recording gages strategically located on the system.

Backsiphonage occurs when a series of conditions exist simultaneously: (1) negative pressure at a water-using "fixture"; (2) faulty fixture connection, i.e., cross connection; and (3) open or leaky control valve between the water pipe and the fixture.

Negative pressure will more commonly occur at the highest points in buildings or community distribution systems. In buildings, negative pressure can also occur because of inadequate hydraulic capacity of the building piping system. Thus, water use on the lower floors of a building may cause siphonage of water in the upper floors of that building. Similarly, in hilly terrain, high water consumption or main breaks may result in negative pressures developing at higher points in a community distribution system. Water service to facilities at ground elevation, where the general terrain is level, presents, at worst, a low-order backsiphonage hazard. An example is water service to lawn sprinklers. High-order backsiphonage hazards may result from improper connections to bedpan washers, toilets, laboratory sterilizers, siphon ejectors, and certain other laboratory facilities.

Cross-connection control programs should include, as one major element, the policy of requiring either air-gap separation or installation of an approved backflow prevention device at the water purveyor's "point of delivery" to premises where "pumping hazards" exist. Further, in some instances, protection at the point of delivery may be required at premises where major backsiphonage hazards exist, particularly at industrial premises. For example, plating works are notorious for repeated installations of submerged inlets (via pipes or hoses) into tanks and vats. Some water utilities have dealt with this problem by frequent and periodic inspections of such premises to ensure elimination of submerged inlets (such a program may be feasible only at small plating works). Other water utilities have categorically required installation of a backflow-prevention device at the water service to every plating works. This example illustrates two basic methods of dealing with cross-connection hazards: elimination of the hazard by a program of internal elimination of the objectionable practice with continuing surveillance; or by development of an air gap or installation of a mechanical backflow-prevention device at the service connection.

Tanks and Reservoirs

Improperly protected distribution-system tanks or reservoirs can contribute coliform bacteria to a distribution system in several ways. Reservoirs might have no covers; the cover might be poorly constructed, thus permitting leakage; covered reservoirs might be subject to windblown materials entering through vent openings, screened or not; and ground storage reservoirs might be subject to surface runoff or underground seepage. The 1929–1930 APHA Committee on Water Supply, considering the problem of bacterial aftergrowths in water distribution systems, questioned the wisdom of using open reservoirs.[1]

This committee made the following statement:

> The committee would urge that more study be given open reservoirs throughout the country by the various water departments with the hope of reducing the number to a minimum. Enough information is now available to throw doubt on the wisdom of using open reservoirs without continuously chlorinating the water. *B. coli* growing on microorganisms does not constitute a menace to health, but if we become accustomed to assuming that bacterial increases in the distribution system are natural growths and of no significance the occasional occurrences of real pollution will also be ignored.

The subject of potable water storage reservoirs has been thoroughly discussed in the AWWA report of the Committee on Open-air Reservoirs.[2] This report discussed replies from 53 communities to a questionnaire. These replies indicated that there was widespread pollution of open reservoirs due to gulls, ducks, and other birds; animals and rodents, such as dogs, cats, mice, rats, and frogs; windblown and atmospheric contaminants; humans, from bathing, fishing, and drowning; and many other sources. Correspondence to the committee showed that night swimming and fishing, particularly in large or isolated reservoirs, were extremely difficult to prevent, even with fences and watchmen. Wires strung across reservoirs to keep gulls and ducks away provided perches for swallows, starlings, and other small birds.

Covered reservoirs might not adequately protect water quality if the covers are improperly constructed and are not watertight. Poorly constructed reservoir roofs can be worse than no roof, as far as contribution of degrading materials is concerned. As for bird contamination, there is a growing realization of the possibility of disease transmission by bird droppings. An outbreak of salmonellosis in Alaska was attributed to sea gull contamination of a domestic water supply reservoir located on a hill not far from where sea gulls had access to bay waters contaminated by raw sewage. Covered reservoirs located in windy and dusty areas can be subject to windblown dusts that contribute significant numbers of coliform organisms to water in the reservoir.

There is a growing trend to use the roofs of large surface-storage reservoirs in urban areas for secondary purposes. Reservoir roofs are used for automobile parking, tennis courts, golf courses, and landscaped areas; some reservoirs have been located under city streets. Special design features are necessary to prevent degradation of water in these reservoirs.

Another hazard is the possibility of surface runoff draining into inadequately protected storage reservoirs. Worst of all is the hazard of direct sewage contamination by leakage from sewers located above ground storage reservoirs. It is obvious that such hazards should be carefully sought out and completely removed. Furthermore, drains from reservoirs to sewers must not be directly connected such that it would be possible for sewage to flow from the sewer into the reservoir under any possible circumstances.

Main Disinfection

The necessity for effective disinfection of newly laid mains or repaired old ones has been recognized by AWWA in the promulgation of *Standards for Disinfecting Water Mains.*[3] M. P. Crabill, chairman of the committee that developed the 1954 standards, stated, "No one will deny the need for the disinfection of newly laid mains, or repaired old ones where samples of the water fail to meet public health standards." Repeated experience in many water systems demonstrates the necessity for an adequate disinfection procedure. Moreover, adequate disinfection depends on a good main-flushing procedure as part of the disinfection operation.

The AWWA standards (C601–68) describe procedures for protecting the cleanliness of the pipe in the process of laying, call for a preliminary flushing of new lines and, finally, specify chlorination to produce a residual of at least 25 ppm after 24 hr of standing in the treated pipeline. Procedures are also described for disinfecting repaired lines. These standards, in combination with the *Standards for Installation of Cast-iron Water Mains* (AWWA C600), approve only rubber rings, asbestos rope, or treated paper rope as yarning or packing material. Jute and hemp packing materials are prohibited. These latter materials generally contain coliform organisms and are extremely difficult to disinfect. Such contaminated packing, while perhaps not constituting a public health hazard, contributes to a continued coliform contamination of water flowing in new mains, despite all reasonable efforts to disinfect lines.

Mains Near Sewers

Water mains located close to sewers, either in parallel or intersecting lines, are a matter of concern in maintaining safe water in the distribution system. If negative pressure develops in leaky mains lying in sewage-saturated ground, sewage can grossly contaminate the mains. The Public Health Service recognizes this problem in its *Handbook on Sanitation of Railroad Servicing Areas*[4] with this statement:

> Where underground water and sewer pipes cross, it is recommended that water piping be installed above the sewer lines whenever possible. If it is necessary for a sewer line to cross above or less than 6 ft. below, it is recommended that the sewer line be constructed of extra heavy cast-iron pipe with leaded joints, for a distance of 10 ft. on each side of the water line. If the sewer line is laid parallel, it is recommended that the water pipe be above and at least 10 ft. from it.

California standards of minimum requirements for safe practice in the production and delivery of water for domestic use state in part:[5] "It is recommended that water pipes be laid as far as possible from and [at] a higher level than sanitary sewers, but in no case shall they be laid in the same trench."

Blowoffs and Vacuum Relief Valves

Distribution-system water quality can be adversely affected by improperly constructed or poorly located blowoffs or vacuum or air relief valves. Blowoffs located where they can be submerged in degraded waters or directly connected to sewers represent extremely objectionable conditions. Vacuum or air relief valves located in sumps subject to flooding or valves permitting intake of dusty air can also adversely affect water quality.

Negative Pressure

Negative pressures have been briefly discussed with relation to cross-connection control. Negative pressure can result in backsiphonage or can cause leakage of contaminated water into water mains. Several causes of negative pressures in distribution systems have been previously listed.

Another cause might be booster pumps taking suction from a main. A report[6] to the Conference of State Sanitary Engineers commented:

> Booster stations on the distribution system should be so designed and located that they will not cause a negative head in the distribution piping. In some cases, it may be necessary to provide a receiving reservoir from which the water can be drawn instead of taking suction from the mains. We do not favor approving plans where booster pumps are to be directly connected to a distribution system main. We much prefer the use of intervening reservoirs from which the booster pump will take suction.

The construction of a basin from which the pump can take suction will correct this problem.

Negative pressures can also be the result of planned or unplanned shutdowns resulting from breaks in mains or efforts to correct excessively leaky lines. Both situations indicate the necessity for a pipe-replacement program. Reduction of low or negative pressures might require development of a more adequate supply of water, additions of major feeders in the transmission system, and the addition of more and better-located control valves.

Aftergrowths

When all other possible causes of coliform contamination have been excluded or eliminated, and coliform organisms are still present, attention turns to the possibility that coliform bacteria are developing in the distribution system. This is the most complex and least understood cause of coliform contamination. Such terms as "aftergrowths" or "secondary growths" have been used. A number of articles in water supply literature report experiences with development of coliform organisms in distribution systems where water at the source meets Public Health Service bacterial standards, and other causes of contamination of the water appear unlikely.[7–16]

It is likely that reported cases represent only a small fraction of the difficulties experienced with coliform development in distribution systems.

Phenomena contributing to this problem are neither well identified nor fully understood.

Understanding is enhanced by an awareness of the nature of the environment within a system of pipes. Most important is the relative vastness of the interior surface of the mains (1 mile of 6-in. main provides about 8,300 sq ft of surface). This surface offers opportunities for a multitude of physical, chemical, and biological phenomena and for the resulting products to accumulate; thus, subtle, insidious changes in the mains are difficult to avoid. The fundamental nature of the microenvironment at the pipe-water boundary is responsible for this. At the interface, the flow of water is virtually nil. Conditions in this filmy zone are markedly different from the open spaces of the main. Absorption and diffusion processes occur here.

The concentration of water-abstracted materials can be much greater than that in the transient flow; for example, concentrations of organic materials and trace elements might be several hundred times that in the moving water.

The environment of the flowing water can be definitely aerobic while anaerobic conditions prevail at the pipe wall. This explains why incompatible reactions can occur within the mains. The chlorine-wasting characteristics at the pipe wall must be taken into account, as well as the fact that the boundary layer interposes a barrier that protects imbedded organisms from disinfecting attack.

The relationship between the amount of flow and the area of main surface is another significant fact. As the relative surface is considerably greater in the smaller mains than in the larger ones, quality conditions in the smaller mains are likely to be more acute. The phenomena described above lend themselves to more intensive development in smaller mains.

It is commonly observed that chlorine demand in summer is considerably greater than it is in winter. Summer residuals, even when the dosage is significantly increased, do not carry as far into the distribution system as they do in winter. Higher temperatures tend to increase the speed of reactions, including the chlorine-wasting reactions. The effect of temperature on biological activity is well known. Within the usual limits of water-supply temperature variations, metabolic activities range from inhibition to peak levels. Various investigations have indicated an association between the frequency of detection of marginal coliform organisms in distribution samples and a summer water-temperature range.

Biologic decompositions in the mains are also provoked by summer temperatures. The temperature factor might provide a major clue to the discovery of the cause of unsatisfactory water quality conditions. But one should not expect a general condition *always* to develop in association with overall changes in temperature, for other *predisposing conditions must be present in addition to the temperature factor.* The critical combination of conditions is likely to be more or less isolated in "sore spot" areas. These should be located by careful field investigations. The passage of a few coliforms past the treatment process, the development of slime growths such as crenothrix in distribution systems, the accumulation of organic matter, water temperatures above 60 °F, the introduction of unfiltered surface water into distribution systems, the existence of noncirculating zones in midsystem, the existence of dead ends, and lack of a systematic mainflushing program appear to be some of the significant contributing factors.

Algae from unfiltered surface supplies or from open distribution reservoirs can provide great quantities of bacterial food. Coliform organisms can develop in deposits of turbidity lying in lines, can develop in conjunction with slime growths in lines, and can develop when various other environmental factors are favorable, such as low velocity or temperatures above 60 ° F. Levin, et al.,[17] assessing the nature of organisms surviving routine water purification processes, concluded that:

> The fact that the incidence of . . . coliform bacteria encountered in distribution systems is sometimes higher than at the water treatment plant effluent . . . is not due to recovery of cells partially injured by chlorine, but rather to the existence of points in the system where gas-producing bacteria find favorable conditions for growth.

The presence of high coliform concentrations in dead ends, in noncirculating zones, and throughout the system during summer when water temperatures are higher, seems to confirm the hypothesis that coliform organisms escape treatment processes and reproduce in a favorable environment. The dearth of data in the literature indicates a need to gather more information to evaluate this phenomenon.

Methods of controlling this problem are implied in some of the contributing factors listed above. In addition to better treatment at the source, eliminating noncirculating zones in the system, and adequate flushing, an important means of controlling aftergrowths is chlorine treatment. It is likely that complete control of coliform aftergrowth is obtained only if chlorine residuals are carried to extremities of a distribution system. This has been accomplished on increasing numbers of systems, but often with difficulty and with consumer dissatisfaction, at least for an initial period.

The universal maintenance of chlorine residuals throughout distribution systems is a controversial subject not agreed on by public health or water-supply experts. The nature of the controversy is indicated in a panel discussion[18] in which several speakers presented data or opinions in support of using chlorine residuals carried to the ends of a system. The argument against universal maintenance of chlorine residuals in water systems is contained in a report[19] of the National Academy of Science–National Research Council (NAS-NRC). In part, this report states:

> Residual chlorine in the concentrations routinely employed in water utility practice will not ordinarily disinfect any sizable amount of contaminating material entering the system, though this will depend on the amount of dilution occur-

> ring at the point of contamination, on the type and concentration of residual chlorine, and on the time-of-flow interval between the point of contamination and the nearest consumer. . . . It is the opinion of the NAS-NRC that the establishment of a universal standard for maintaining residual chlorine in water in distribution systems is not desirable. . . . The NAS-NRC does not consider maintenance of a residual a satisfactory substitute for good design, construction, and supervision of a water distribution system, nor does it feel that the presence of a residual in the system constitutes a guarantee of water potability.

Water-utility management and those responsible for water quality should not hastily resort to chlorination as the easy way out for all coliform contamination problems. Chlorination should be used to deal with coliform and other biologic water quality problems that cannot otherwise be dealt with, after reasonable efforts have been made to locate and remove the basic cause of the problem. Chlorination is not a substitute for an active cross-connection control program; it should not be used to cover up other defects or as a substitute for preventing entry of turbidity and organic matter into the distribution system. Where laboratory analysis shows that water in the distribution system is contaminated, investigation should be made to locate the cause, and appropriate corrective steps should be taken.

ENGINEERING AND OPERATION

A number of factors in system design, construction, and operation affect the maintenance of water quality. These include treatment at the source, system layout, selection of pipe material and protective coatings, system valving, tanks and reservoirs, and various operation and maintenance practices.

Quality Control at Source

It is generally conceded that the quality of water in the distribution system will not be superior to the finished water at the point of production and treatment. Further, the quality of the finished water is predicated in good measure on the quality of the source. Each community tries to obtain the best natural source available, that which requires a minimum of treatment and control.

A concomitant strategy of control is practiced to achieve a general leveling in the compositional characteristics so that a highly uniform water can be delivered to the consumers. This is important to industries in which water often plays a major role in processing.

The value of delivering raw water of relatively optimal and uniform quality to the treatment plant should also be obvious. It is conducive to orderly treatment procedures, facilitates control, and is an important factor in assuring efficient and reliable results. Quality control at the source also tends to smooth out plant loads and to spare the plant from shock loads and excessive stresses.

Where quality control at the source is not practiced, the effects of treatment irregularities are likely to be passed on, to a greater or less degree, to the distribution system. This is often the case with water supplies having streams and uncontrolled watersheds as their sources. The modern treatment plant can do a remarkable job, but flashiness, shock loads, and unabated pollution continue to impair its performance. The ability and capacity of its performance is often so vaunted that a greater tolerance toward pollution and other disturbing factors in the source is in danger of being encouraged. Any type of supply stands to benefit from pollution prevention and abatement programs at the source.

General Layout of System

Provision for circulation, or lack of such provision, will have some effect on water quality. Here again, its effect will largely depend on the quality of water entering the system. Lack of circulation obviously creates dead ends with their variable and somewhat unpredictable problems.

Selection of Pipe Material and Protective Coatings

Noncorrosive waters create no problem, but corrosive waters require a consideration of the factor for reasons of water quality. Either a noncorrosive pipe material must be selected or the pipe must be lined with a protective material. Use of pipe coatings or noncorrosive pipe does not, however, fully dispose of the problem, since corrosive water can attack the consumer's piping system. Corrosion, at whatever point it occurs, will produce corrosion products which will degrade water quality in large or small degree, depending upon the particular circumstances.

Air Relief Valves and Blowoffs

The location of air valves or some form of air-bleeder valve is important to relieve entrapped air. They help prevent milky water when lines are filled. Normal good practice in the rest of the design should prevent water quality problems due to air. Vacuum-release valves are installed to allow the entrance of air to prevent collapse or damage to a line not capable of withstanding atmospheric pressures when under vacuum. These valves have no effect on quality except as a preventive measure in reducing the possibilities of breaks. They should be so located and protected, however, as to prevent the entrance of contaminated or polluted water when they are open. Vacuum valves often leak when under very low head, and such leaks might submerge the vacuum valve with water if proper drainage is not provided and maintained where installations require it. Although blowoffs are normally located at a low point for the purpose of draining a line or of connecting lines, they should also be provided where there is no other means of blowing off a dead end. The blowoffs do not directly affect water quality, but if they were not present to permit blowing off a line, it might be impossible or difficult to correct a poor-quality condition or at least to give temporary relief. Blowoffs should not be constructed to allow a contamination hazard such as a direct connection to a sewer or sewer manhole structure.

Tanks and Reservoirs

Tanks and reservoirs offer frequent opportunity for water to be polluted. In these facilities, water is not normally under pressure; the facility is never completely tight and is often completely exposed to various sources of pollution.

Open reservoirs can be subject to algae growths, either floating or attached to walls. Unlined reservoirs are subject to weed growths; even lined reservoirs where sedimentation occurs can support weed growth. Open reservoirs are subject to bird contamination, airborne pollution, and, to some extent, debris thrown by people. Covered tanks and reservoirs must have tight roofs, or the water can become contaminated by leakage during the rainy season. Vent areas must be protected so that roof drainage cannot be deflected through openings. Vents should be protected from windblown contamination, particularly in landscaped areas where fertilizers might be used.

Wood roofs require sufficient vent area for adequate ventilation to prevent dry rot. Concrete reservoir roofs do not have this problem, so vents should be kept to a minimum. Local conditions will dictate design, but the area should be screened for protection against vandalism. Furthermore, the vent areas should be protected to prevent rain, windblown roof drainage, debris, and as much as possible, dust and dirt from entering the reservoir. All can be accomplished with a properly designed and installed louver. No protective coatings, preservatives, or joint sealers that would impart taste, odor, or toxic chemicals to the water should be used in tanks or reservoirs.

Operation and Maintenance Practices

Some of the practices that should be followed in operation and maintenance are:

1. Make operating changes in water control in such a manner as to prevent sudden changes in velocity that might stir up sediment and make the water dirty.
2. Avoid flow reversals in pipe not normally subject to flow reversals if it is suspected that the pipe contains considerable sediment.
3. Avoid allowing reservoirs to get so low at times of heavy draft that vortexing and entrainment of air can result.

4. Beware of hydrant-testing programs; when they are necessary, be prepared for complaints of dirty water. Program the testing to suit the system best, notify consumers, and clear the system areas involved as soon as possible after the test.

5. Determine whether the distribution piping system contains deposits of settled material.

6. Set up a main-flushing program commensurate with the need of the system. Such a program for a given water system might require nothing or might require routine blowoffs of the entire system.

7. Set up a routine program for flushing dead ends where chronic complaints occur.

8. In distribution areas having considerable deposits of sediment, where spot blowoffs in response to complaints are not adaptable because of the dirty water that would result, expedite a complete flushing program. If this is not possible or practical, the maintenance of a chlorine residual should be attempted to inhibit bacterial decomposition of the deposits with resulting "dead-end" type of quality deterioration.

9. Determine whether tanks and covered reservoirs have roof leakage and entrance of windblown dust, dirt, and debris. In this way many sources of pollution can be eliminated.

10. Determine whether deposits are forming in tanks and reservoirs. Set up a cleaning program in accordance with the needs.

11. Maintain adequate records of complaints of water quality. Proper utilization of complaints is an important adjunct to water quality management in distribution systems. Proper follow-up on complaints provides valuable information on water quality problems in distribution systems.

NUISANCE ORGANISMS

A number of larger biologic forms may find their way into domestic water distribution systems. Broadly, these are known as nuisance organisms and include nematodes, snails, the larvae of the chironomid fly, and others. Some authorities also include *Crenothrix* under the general heading of nuisance organisms. Snails and nematodes are introduced at the water source and can best be controlled at that point.

Chironomids

Water systems are occasionally invaded by small midge larvae, the best known of which, because of their characteristic color, are sometimes referred to as "bloodworms." The insect forms most frequently giving trouble are the aquatic stages of the gnat-like flies of the family Chironomidae. These are true flies belonging to the order Diptera. Chironomids are represented by many species and are virtually of worldwide distribution from the Arctic to the tropics.

Measures for the prevention and elimination of larval infestations may be divided into mechanical, biological, and chemical procedures.

Mechanical Methods. The best mechanical method for control of chironomids is that of covering the reservoir with an insect-tight roof. The adult midge, being small, can crawl through cracks and small openings to reach the water and deposit eggs, so the cover must be quite tight.

Covering reservoirs and screening all vents and openings in the cover with 20-mesh screen will prevent most species of midges from gaining access to the water in storage to lay eggs. Where exclusion of adults cannot be accomplished other means of control and elimination may be provided.

Excelsior filters have been used to prevent *Cyclops* and *Daphnia* from gaining access to distribution mains and should be equally successful in excluding chironomid larvae. Such filters can be easily built, and placing them in position is usually no major problem. During the 1930s a combination sponge and excelsior filter was placed over the outlet pipe in a 15-million-gal distribution reservoir in western Pennsylvania. The filter consisted of a wooden frame covered with chicken mesh wire and (fairly loosely) filled with sponges and excelsior. It proved effective and immediately stopped crustacea from appearing in water drawn from household taps on the system. This filter remained in place for over a year, long after it was required, without any undesirable effects.

During the summer of 1945, similar filters were successfully employed in two instances, one in western Pennsylvania and another in Rhode Island. The offending organisms were, in both cases, crustacea. In Rhode Island, the excelsior filter was used in a steel basin 20 ft high and lowered into place from the top. The filter prevented organisms from entering the mains, and by drawing water from the bottom of the tank, the crustacea, which tend to stay near the bottom, were finally eliminated.

In western Pennsylvania, the filter employed was braced against the 16-in. suction main feeding a booster pump. This filter effectively stopped the crustacea from entering the system.

Frequent cleaning of reservoirs will prevent accumulation of an abundant food supply for larvae, snails, and other undesirable organisms and in this way will lessen the chances of trouble. Although experiments by the Public Health Service have demonstrated that chironomids will deposit eggs upon the surface of clean tap water in a bucket and larvae will develop in the absence of visible sediment or obvious food supply, the cleanliness of reservoirs is an important factor in reducing the frequency and magnitude of such infestations.

Biological Methods. Naturalistic methods of control depend for their success on the interruption in some manner of the biological development of the insect. Examples of this type of control include such methods as:

1. Removing a major source of food supply of the larvae by controlling algae. This is particularly true on sloping and shallow reservoir walls.

Rolling large crystals of copper sulfate down such slopes has been found more effective for this purpose than applying the chemical in the conventional manner.

2. Stocking the reservoir with bottom feeding fish.
3. Emptying the reservoir, when this is possible, and keeping it out of service for several days to eliminate one generation of midges by destroying the eggs and larvae.

Chemical Methods. Chironomid larvae have survived chlorine concentrations as high as 50 ppm with a contact period of 24 hr. Copper sulfate at 50 ppm has been reported ineffective.

At Peoria, Illinois, chironomid larvae retained their activity for a period of over an hour in a rough qualitative test in which large excesses of hydrated lime, copper sulfate, and HTH were added to water in which larvae were present. Chemical treatments ordinarily used in waterworks operation are not effective, according to these reports, in the control of chironomid larvae. It was found that rendering the water acid (a pH of 2.0 to 4.0) or alkaline (a pH of 8.5 to 10.0) had a killing effect. It was also found that 3 ppm of an insect powder containing pyrethrum was effective.

In August, 1945, chironomid larvae were discovered in the distribution system and in the two open clear-water storage reservoirs at Alexandria, Virginia. The larvae developed in water containing chloramine residuals of 0.6 to 1.0 ppm with an average retention period in the reservoirs of about 3 days. Laboratory tests showed that these larvae were resistant to chlorine and copper sulfate. Copper sulfate applied to the reservoir water (containing 0.6 to 1.0 ppm chloramine residual) at the rate of 4 lb per million gallons had no effect upon the organisms. On August 31, 0.01 ppm of DDT was applied to the water in the two reservoirs. Killing results were somewhat slower in the reservoir than observed under laboratory conditions; however, 3 days after the application of DDT, the larvae disappeared quite suddenly.

The use of chlorinated hydrocarbon insecticides to control larvae infestations in domestic water supply reservoirs *cannot* be recommended as a standard procedure. While DDT used at a dilution of 0.01 ppm has been shown to be effective in several control demonstrations, *its use should be considered only in unusual cases and it should not be used without prior approval by public health authorities.*

In general, each situation requiring control must be evaluated independently. In some cases minor mechanical adjustments may successfully neutralize the problem. In others, a combination of physical and biological adaptations may be required to effect the desired balance in a reservoir or to eliminate larvae from water systems. Even the most reliable chemical measures available at this time offer only temporary relief, and their application should be limited to emergency situations or to situations where all other methods have failed.

Crenothrix

Crenothrix, one of the higher bacteria, is a microscopic, filamentous (threadlike) organism closely related to true bacteria and microscopic fungi. This organism will live in the dark and in the absence of dissolved oxygen but will not thrive in water containing large concentrations of dissolved oxygen. It requires iron as an essential food and thus will live on the inside of distribution systems conducting water containing iron.

Crenothrix will grow in gelatinous masses on the inside of water mains to an extent that will seriously reduce the capacity of the mains and will lead to the presence of objectionable concentrations of precipitated iron in the water and to objectionable tastes and odors, especially when the organism dies. Its presence is to be anticipated when well water containing iron, but little or no dissolved oxygen, is pumped into distribution systems.

Crenothrix may be eliminated by removing iron (food) from water before it enters distribution systems, by increasing the concentration of dissolved oxygen in the water above about 2.0 ppm through aeration, and by the application of copper sulfate or chlorine to the water. It is significant to note, however, that the doses of copper sulfate and chlorine required for the *rapid* destruction of these organisms are higher than may be utilized in the treatment of a potable supply, but fortunately limited doses are effective *if continued for a period of several weeks or more.* Copper sulfate doses in excess of 0.3 ppm are effective, and a dose of 0.5 ppm is recommended. The chemical may be applied with various types of feeders available for applying alum to water.

The chlorine dose required to destroy this organism is that dose necessary to result in a concentration of *residual chlorine* between 0.5 to 1.0 ppm. It may be quite difficult to maintain this concentration of residual chlorine unless ammonia is added also to stabilize the chlorine. Even then, objectionable tastes are likely to be produced through the destruction of the organisms, so such treatment should be preceded by a notice to the consumers that special treatment is to be utilized for the destruction of these organisms so they will not be unduly concerned as to the quality of the water supplied to them temporarily.

SAMPLING

Distribution System Sampling

An effective sampling program is essential for the proper maintenance of quality in the distribution system. Most systems base their programs on the recommendations established by the Public Health Service *Drinking Water Standards.* The standards are concerned primarily with bacteriologic quality—more specifically, with coliform organisms. The standards recognize that requirements are affected by the source of supply, the character of treatment, sanitary conditions in the distribution system, average consumption of water, and the population served. The diversity of water-supply systems makes it difficult to lay down hard-and-fast specifications. The major specification prescribes the minimum number of samples to be examined monthly. It is also stated that the samples should be representative. The minimum number of monthly samples required ranges from two, for populations under 2,000, to 500, for populations up to 5 million. Nothing is specified about the number of sampling points and the actual frequency of sampling. The qualification of representative sample is open to much speculation and opinion.

Just what pattern should the sampling program take? When sampling programs of various communities are examined, it is not always possible to tell whether they conform to a meaningful plan or are made according to matters of convenience. The collection of samples from a tap at city hall, a prominent public building, or the treatment plant operator's home might coincide with some plans, but often this is not the case. The frequency of sampling from various points can also be similarly faulty.

Laboratory service capacity, personnel, time, economic factors, and policy attitudes all limit the sampling program. In a practical sampling plan, it is not feasible to cover the multitude of hypothetical situations that can be attributed to the distribution system.

Sampling points should be selected, in part, to trace the course from the finished water source to the prime conduit and, then, through the major and minor arteries of the system. Such sampling points may be regarded as primary. The sampling point on a minor artery, or on an active main directly connected to it, would be representative of water quality being furnished to a subdivision of the network. Generally, primary points should qualify as official sample stations mutually acceptable by water and health authorities for evaluating quality according to prevailing health standards. Primary points along transmission and major arteries can also be included with official stations, wholly or in part, if this is indicated for a specific community. The number of distribution subdivisions should be reflected by the number of official sampling stations required for the specific community. Determining the number and location of such points requires careful study.

A first estimate of the sampling points can be based on the Public Health Service requirements for bacteriologic quality. According to the size of community, the number of samples to be examined monthly divided by the frequency of sampling should indicate the number of points. Thus, if official samples are to be examined weekly (a customary practice), the number of sampling points should be approximately one-quarter of the monthly samples. Assuming the indicated number of samples for a community is 100 per month, the corresponding number of sampling points should be about 25, on a weekly examination basis. The problem is then to select 25 points in the distribution system capable of equitably representing the quality of water being served to the consumers, from which daily samples may be taken on a rotating basis, e.g., approximately four samples per day, seven days a week.

A first temptation in formulating a sampling plan would be to divide the community in the example above into 25 uniform geographic areas and stick a sampling point into the center of each. Only by sheer coincidence can such a plan prove meaningful. The community is a heterogeneous complex and bears no direct relationship to the general geography. The same may be said for the relationship of geography and the distribution system.

In developing the sampling plan distribution, associated auxiliary structures such as standby pumping stations, boosters, storage tanks, and regulators should be considered. If they are likely to affect the official results, additional official stations might be required or specific provision made in the auxiliary sampling program.

Official Sampling Stations

Obtaining an officially correct sample from the distribution system is not as simple as it might seem. One would think almost any tap in a specified area would do, but experience has shown otherwise. Local conditions at the tap and in its connection to the main can make the point unrepresentative of the quality of the water being furnished to the consumers.

The truest evaluation of water quality can be obtained from samples drawn directly from the main. It would then seem that samples taken from hydrants should prove satisfactory, but it is well known that this is not true. The fault lies with the construction of the hydrant, its unpredictable usage, and the manner of its connection to the main.

The most critical requirement for samples is that they be representative for coliform bacteria in the flow. Because of the great sensitivity of the test and of the possibilities for false interpretation, it is necessary to exercise extra care and to standardize the procedure as much as feasible. After many years of dealing with the problem, the water department of New York City decided that the establishment of official sampling stations of special design would contribute significantly to the resolution of the various difficulties.[19] A sampling station was devised that approached the theoretical requirements. These were constructed and installed at primary points in the distribution system. The stations are also used for evaluating water quality in order to meet the Public Health Service Standards. The features of design are:

1. A direct connection with the shortest pipe possible to the main being sampled.
2. A connecting pipe of corrosion-resistant material.
3. A drip valve to drain the sampling line when it is shut down. This is intended to avoid freezing during the winter months. The valve is located below the frost line and operated by an extension bar that extends into the sampling cabinet.
4. A sampling line and extension bar enclosed in a standpipe below the sampling cabinet. These structures are made of cast iron, but lighter structures may be preferable.
5. The sampling cabinet enclosing a single gooseneck sampling tap and a porcelain-lined metal drain bowl. The cabinet has been made larger than required with a view toward accommodating recording or other equipment in the future.
6. The entire unit is sturdily constructed to withstand tampering. It is located in the street close to the main to which it is connected, and is accessible at all times.

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16

Treatment of Water for Cooling, Heating, and Steam Generation

By SIDNEY SUSSMAN

INTRODUCTION

Water already satisfactory for domestic use frequently requires additional treatment when used for cooling, heating, or steam generation—applications which accounted for more than 102,000 mgd of the 20,600 mgd municipal and 140,000 mgd private industrial water supplied in 1960 and whose use continues to increase. The many technical and nontechnical considerations which must be evaluated when selecting the water treatment needed for such systems are far too extensive and complex to be presented fully within the confines of this chapter. However, the widespread need for information about boiler and cooling water treatment makes it important for technical and operating personnel in the public water-supply industry to have some acquaintance with this specialized area.

This chapter, therefore, surveys the types of cooling, heating, and steam-generating systems, the water-caused problems which can develop in each of them, their water quality requirements, and the treatment methods available for establishing and maintaining the necessary water quality.

It will be noted that there are many similarities to municipal water-treatment practice, but the differences are even more numerous. There are many similarities between the problems caused by the treatment of cooling waters and of boiler waters, but again there are more differences. The complexities of water problems in these areas have been deliberately emphasized in this chapter in order to counteract a common tendency toward their oversimplification.

Each cooling, heating, or boiler water problem deserves careful and complete examination of *all* pertinent factors before reaching a conclusion on the best method for handling it. Contrary to widespread opinion, the composition of makeup water and the desired quality of the cooling, heating, or boiler water do not provide sufficient information for setting up a water-treatment program. A knowledge of equipment construction and operation is necessary even to select a suitable treated-water composition. Other considerations which significantly influence the choice of water-treatment chemicals, equipment, and standards include the design of the water-using system, materials of construction, operating details, equipment location, and both quantity and quality of available operating labor. Even this list is not complete for all cases.

For best results, water treatment for steam generation, cooling, heating, and industrial process systems should be selected by and carried out under the supervision of a specialist experienced in industrial water technology. In addition, it is impossible to emphasize too strongly the importance of regular and effective control of the water treatment if a system is to operate free from water-caused troubles.

SYSTEMS AND APPLICATIONS

The systems whose water problems and treatment are discussed in this chapter include a great diversity of types and a tremendous range of size. Cooling water flows may be less than half a gallon per minute for a home air conditioner, or a river-sized amount for a large oil refinery. Steam-generating water treatment differs greatly according to whether the boiler is operating at less than 5 psi for heating or above 3,209 psi (critical pressure) for electric power generation. Heating-water problems are quite different in a residential radiant hot-water (180 °F) heating system and in a high-temperature (400 °F) hot-water system serving the far-flung buildings of a modern airport.

Cooling water may be used in a once-through system or may be recirculated in either an open or closed circulatory system. The kinds of water problems which develop and the economics of treatment depend upon the type of system, among other factors.

As the name implies, once-through cooling systems do not reuse water.

After passing through such a system, water taken directly from larger surface sources (lakes, rivers, or the ocean) is usually returned to the source at a location which will minimize short-circuiting of the warmed effluent water to the intake. Well waters after use in such systems may be discharged to surface-water courses or to recharge or diffusion wells. Smaller systems, particularly those supplied from public water sources, may discharge to sanitary or storm sewers. The large volumes of water used in once-through cooling systems normally preclude the application of any but the most inexpensive water treatment.

Open recirculating systems include various types of evaporative coolers, such as spray ponds, cooling towers, evaporative condensers, and chilled-spray dehumidifiers. Because of changes in water composition which take place during the recirculating process, treatment for the circulating water in these may be quite different from that which might be anticipated on the basis of the makeup water composition. The changes include increased dissolved-solids content resulting from evaporation, constant resaturation with oxygen and other gases from the air, and scrubbing from the air of solid matter, including bacteria and spores. Indeed, in this type of system water problems may depend as much or more upon content of the air coming into contact with the recirculating water as upon the composition of the makeup water.[1]

Closed recirculating systems are often erroneously believed to be completely free of water-caused problems. They would be free of such problems if they were truly closed, but experience has shown that a considerable proportion of them regularly operate with appreciable water loss and replacement.[2] Impurities introduced with the makeup water create operating problems which require water treatment.

The most common cooling-water systems are refrigeration systems for meats, dairy products, and frozen foods in local markets. Their larger counterparts serve quick-freezing plants, commercial cold-storage warehouses, ice-manufacturing plants, ice-skating rinks, and industrial refrigeration applications.

A closely related use of cooling waters is in air conditioning, which has been the fastest-growing cooling-water application in recent years. Air-conditioning systems use water for closed chilled-water systems, for dehumidification and humidification spray systems, for direct cooling of air, and for refrigerant condensation. The water circuits can vary in a typical central air-conditioning system equipped with mechanical refrigeration. Once-through cooling water may replace the cooling tower in one application; both the cooling tower and the refrigerant condenser may be replaced by an evaporative condenser; or the cooling may be done by absorption refrigeration.

Without question the largest volumes of cooling water are used for industrial applications, which range from direct quenching of hot coke or steel in major steel mills to the cooling of milk in small dairy plants. Cooling water includes steam condensation in power plants, cooling of plastics manufacturing molds, diesel engines, oil-refinery heat exchangers, and an almost infinite number of other applications. Large industrial establishments are usually well aware of potential cooling-water problems and are prepared to meet them both technically and economically.

Steam generation water-treatment requirements are affected by the boiler operating pressure, makeup rate, heat-transfer rate, construction details of the boiler and its auxiliaries, and the uses to which the steam is put, as well as the analysis of the makeup water.

Steam-heating boilers for residences and other small structures are the most numerous and, generally speaking, have the simplest water problems. Most of these are cast-iron sectional or steel fire-tube boilers which operate at only a few pounds per square inch of steam pressure and have relatively low heat-transfer rates. The major water-caused problem in these boilers is corrosion, although scale can form when unusual operating conditions lead to excessive loss of steam or condensate. It is not widely enough recognized that much of the corrosion damage in this type of boiler takes place during the summer layup when the boiler is not in operation.[3]

Industrial boilers, the next largest group, include a tremendous variety of types and capacities which operate at from several pounds per square inch to well over 1,500 psi of steam pressure. Most of these are water-tube boilers. They include installations in which all the steam is condensed and returned to the boiler, those in which part of the steam is returned, and those in which none of the steam is returned. A majority of industrial steam systems fall into the last two classes, and the resulting accumulation of dissolved solids from the makeup in the boiler water causes scale formation to be the prevalent water problem in industrial boilers.

Corrosion is also an important factor here, as are related problems caused by the fact that live steam may come into direct contact with items destined for human consumption or with industrial products that are peculiarly sensitive to traces of impurities. Condensate return systems may require protection from corrosion. Altogether, the many variables encountered in industrial steam generators create an almost infinite variety of individual boiler-water treatment problems.

At the opposite end of the steam-generation spectrum from the individual household heating boilers are the tremendous boilers which provide extremely high-pressure steam to drive the turbines used for the generation of electric power in large central stations. These may be operated with virtually no makeup or, when also providing steam for district heating purposes, with a large makeup.

A fairly recent addition to this class of steam boilers is the once-through boiler in which better than 90 per cent of the water may be evaporated during a single pass. These boilers have special water-quality requirements.

Heating water applications have advanced considerably since the early residential use of convection hot-water heating systems. For economic reasons high-temperature hot-water systems may be more attractive than steam for certain installations which cover a wide area, such as single-story industrial plants or airports. In them, the transmission of water at 250 to 450 °F and 30 to over 350 psi pressure provides savings in the construction of heating systems since equivalent steam systems would require much larger diameter steam piping plus condensate return systems. The high-temperature hot water carries heat from the boiler to various scattered locations at which it is converted to low-pressure steam or low-temperature hot water in heat exchangers.

The ordinary hot-water heating system requires treatment in order to correct for the effects of water losses. High-temperature hot-water systems require "single shot" treatment of the large volume of water in the initial fill, followed by treatment to maintain the desired conditions in the circulating water after the system has been put into operation.

Special problems are encountered in the closed water-heating loops of nuclear-power reactors. In these, the presence of dissolved or suspended impurities can result in the development of undesirable radioactivity so that measures to keep the circulating water free of them must be provided.

WATER-CAUSED PROBLEMS

Water problems in cooling, heating, and steam generation derive in large measure from the kinds and concentrations of dissolved solids, dissolved gases, and suspended matter in the makeup water supplied. The normal operation of these systems, however, can bring about substantial changes in water composition. Thus, evaporation, air scrubbing, or degasification can profoundly alter the water in the system, creating problems quite different from those which might be anticipated from the makeup water composition.

Design and construction features of water-using systems can also affect the type and particularly the severity of certain water-caused problems. These effects may be direct, as when a more readily corrodible metal is used, or they may be indirect, as when equipment is so constructed as to make the application of water treatment well-nigh impossible, or when evaporative cooling equipment is so located that the circulating water will absorb large quantities of flue gas.

In the operation of every cooling, heating, and steam-generating system the water changes temperature. Higher temperatures, of course, increase both corrosion rates and scale-forming tendency. Careful investigation of actual operating water temperatures is important. At times, industrial systems involve paradoxical situations, such as the development of higher water temperatures in certain absorption refrigeration machines when they are operating on partial load than when operating on full load.

Evaporation in process steam boilers and in evaporative cooling equipment increases the dissolved-solids content of the water. Depending upon the makeup-water composition and the operating conditions, this increased concentration can become the cause of either scale formation or intensified corrosion unless corrective treatment is supplied.

The effects of air scrubbing in certain cooling waters cannot be overemphasized. In addition to maintaining a corrosive environment by keeping the water saturated with atmospheric oxygen, additional difficulties may be caused by other materials scrubbed from the air. When appreciable amounts of flue gases are present, the circulating water can absorb enough sulfur oxides to become extremely acidic and corrosive after the natural buffering capacity of the water has been exceeded. This action has resulted in very rapid, premature equipment failures. Suspended solid matter may also be scrubbed from the air and can accelerate localized corrosion or damage moving parts. Undesirable organic growths may develop from bacteria and spores washed from the atmosphere.

The two most frequently encountered water problems—scale formation and corrosion—are common to cooling, heating, and steam-generating systems. Scale may form because of the composition of the makeup water, but most commonly develops as a result of further changes occurring during evaporation. Corrosion can take place wherever a metal, water, and oxygen get together, as in almost every cooling, heating, and steam-generating system. In addition to these water-caused problems common to all of the water systems under discussion in this chapter, there are other water-caused problems which are less widespread.

The development of biological growths following the pickup of organic matter from the air in evaporative cooling systems has already been mentioned. There are other important sources of biological problems in cooling-water systems. Thus, the use of river or estuarian waters for once-through cooling often results in the development of objectionable growths of slimes or mollusks. Also, the increasing use of sewage-plant effluent as makeup for some industrial cooling systems has increased their biological growth problems.

One cooling-water problem which may be either chemical or biological in origin is the deterioration of cooling-tower wood. There are actually several types: one caused by excessively high alkalinity or oxidizing substances, such as chlorine, in the circulating water; another caused by fungus action. At first, wood deterioration may only reduce cooling efficiency by changing the pattern of water distribution. Ultimately, however, weakening of wood structural members can lead to collapse of the tower.

The pickup of solid matter has been mentioned as one of the undesirable effects of air scrubbing in cooling systems. Depending upon their physical or biological nature, these solids can cause development of organic growths, intense localized corrosion, interference with heat transfer, or damage to moving parts.

In addition to the formation of scale or corrosion of metal within steam boilers, auxiliary equipment is also susceptible to similar damage. For example, attempts to prevent scale formation within a boiler can lead to makeup-line deposits if the treatment chemicals are improperly chosen. Thus, the addition of normal phosphates to an unsoftened feedwater can create a dangerous condition by clogging the makeup line with precipitated calcium phosphate. At the other end of the steam cycle, corrosion of condensate lines is a common phenomenon, most often resulting from the low pH caused by the presence of carbon dioxide in the steam.

Carbon dioxide is only one factor which may adversely affect steam quality. The carryover into the steam lines of droplets of boiler water containing dissolved salts produces a steam which is objectionable for many applications. Although boiler construction and excessive steaming rates are sometimes at fault in the formation of low-quality steam, such a condition can develop temporarily in any boiler as a result of foaming or priming. Foaming consists of the development of a layer of bubbles on the surface of the boiling water. It may be caused by one or more of several conditions, among which are high dissolved solids and the presence of oil. The latter may enter the boiler with condensate from a steam-driven engine or from a leak in the oil preheater. Priming is a surge of boiler water into the steam; it is a temporary condition often resulting from a sudden increase in steam demand.

Low-quality steam can produce undesirable deposits of salts and alkali on the blades of steam turbines, sharply reducing turbine efficiency. These deposits can be washed off with relative ease. Much more difficult to remove are silica deposits which can form on turbine blades even with steam whose quality is satisfactory by ordinary standards. At steam pressures above about 600 psi, silica from the boiler water actually dissolves in the gaseous steam and then re-precipitates at the lower pressures in the turbines.

Higher-pressure steam boilers are also subject to two forms of corrosive attack associated with high caustic concentrations. Caustic embrittlement or caustic cracking can take place when a hydroxide-containing boiler water is able to concentrate in contact with stressed metal—rivets or rolled tube ends. It rarely, if ever, occurs in boilers operated below 400 psi and is becoming rare with the greatly increased use of welding in boiler construction.

At very high steam pressures, direct caustic attack of the boiler metal is encountered. It seems probable that this, too, may involve concentration of the caustic present in the boiler water.

In hot-water heating systems, corrosion is the major water-caused problem. Damage to single-face mechanical shaft seals on pumps in such systems has been blamed upon water-treatment chemicals, but investigations of many failed seals show that the damage is most often caused by mechanical factors, such as improper installation or abrasion by suspended fine particles of mill scale.

In the closed water loops of nuclear reactors the use of corrosion-resistant metals for piping and equipment and demineralized water for makeup avoids the usual corrosion and scale problems, but other troubles can result from the development of radioactivity in dissolved or suspended materials ("crud") in the recirculating water.

WATER-QUALITY REQUIREMENTS

For municipal use, emphasis is placed upon production of water which is safe to drink, substantially taste- and odor-free, clear, and colorless. Secondary quality standards, considered to be desirable but nonessential, sometimes lead to the reduction of excessive hardness or the alleviation of excessive corrosiveness.

Industrial waters, on the other hand, have quality requirements which are often more stringent than those for potable waters and which vary widely according to both the type of application and the specific installation. As a case in point, it is impossible to give a single water quality specification even for such a common industrial water requirement as steam-boiler makeup. Most city water supplies can be used directly and without treatment for makeup to cast iron steam-heating boilers, if these operate with virtually no loss of steam or condensate. With steel-tubed heating boilers, however, corrosion-control treatment is needed with most waters. Furthermore, scale-control treatment is essential with any boiler of either metal whenever appreciable amounts of makeup water are used—making it the equivalent of a process steam boiler. But water treatment satisfactory for such low-pressure boilers is completely inadequate for use with high-pressure boilers generating steam for production of electricity in a turbine-driven generator. Certain of these require a boiler water which is as free of all dissolved solids and gases as it is possible to make it.

Accordingly, it should be kept in mind that the information given below merely illustrates in general terms the broad scope of water quality requirements for cooling, steam generation, and heating. Remember, too, that the requirements for *makeup* water, that is, the water entering a system—and those for the water in the system—*circulating* water or *boiler* water, as the case may be—must also be carefully differentiated.

COOLING WATERS

Once-through cooling waters should be reasonably free of suspended matter which may clog or settle out in the system and of excessively heavy contamination with living organisms. It is difficult to place quantitative labels upon the quality requirements for these waters. At best, it can only be pointed out that any defects of the available water supply must be correctible by very inexpensive treatment methods because of the large volume of water used. A few specific limitations which have been suggested, and which are equally applicable to open recirculating systems, are that the turbidity be below 50 ppm, iron or manganese below 0.5 ppm, and sulfides (as H_2S) below 5 ppm. The latter are objectionable because of their corrosive effects.

For open recirculating systems, the calcium hardness and alkalinity of the makeup water should be low enough so that a cooling tower can operate with the circulating water equal to at least several concentrations of makeup before scale forms at a significant rate, if the water-saving purpose of a cooling tower is to be achieved. Other quality requirements for cooling-tower makeup water are relatively unimportant because the changes in water composition which take place while the water is circulating through the cooling tower are much more significant in the development of operating problems than is the makeup water composition itself.[1]

The circulating water must be treated to keep it reasonably noncorrosive and non-scale-forming, as well as free from slime and algae growths. It is difficult to be specific about concentration limits for particular constituents in a circulating cooling water, because these will depend in great part upon construction and operating details for a particular installation and upon the type of treatment selected. For example, consider two cases in which corrosion is the major problem. The minimum corrosion rate can be obtained by addition of sodium chromate maintained at 200 to 500 ppm with a minimum pH of 7 for most effective results. On the other hand, lower chemical costs are possible if a slightly higher corrosion rate is acceptable. This can be done by using much lower chromate concentrations (20 to 50 ppm) along with a similar concentration of a coinhibitor, such as a polyphosphate, but in this case the optimum corrosion inhibition can only be obtained within a narrow, lower pH range, generally about 6.2 to 6.8.[4]

For scale control a positive Langelier index of 0.5 to 1.0 is frequently called for, but even limits of circulating-water composition for scale control based upon the Langelier index or the Ryznar stability index will vary according to the maximum temperature in the system, which may range from a 105 to 110 °F for the usual air-conditioning system to 200 °F or higher for cooling waters used in steam condensers.

It is generally considered good practice to limit the total dissolved solids to not over 2,000 ppm in circulating waters of large cooling towers so as to minimize galvanic corrosion in the equipment. When sulfuric acid is fed for calcium carbonate scale control, the alkalinity of the makeup water is usually held at about 15 to 25 ppm, with that of the circulating water in the 50 to 100 ppm range. Other common, but not invariable, limits for circulating cooling-tower waters are a pH of 6 to 8 and maximum suspended solids about 100 to 150 ppm.

In all-wood cooling towers, the maximum chlorine concentration added for slime or algae control is held to 1 ppm and the maximum pH to 7.0 in order to minimize delignification of wood structural members. It is not always economically possible to maintain such restrictions in smaller equipment.

Closed circulating cooling-water systems rarely have sufficient makeup to create serious scale problems, but corrosion is fairly common. For this reason it is desirable to maintain a minimum of 200 ppm sodium chromate in such waters with a pH in the 7.0 to 8.5 range. Diesel jacket and similar closed cooling systems which have higher operating temperatures or must combat cavitation effects often carry a minimum of 2,000 ppm sodium chromate. Suspended matter, particularly abrasive suspended matter, can damage circulating pumps and should also be minimized. This may be done by strainers inserted in the water lines.

STEAM GENERATION

Specific standards of concentration for the various constituents in boiler waters can be more readily established, although these will still vary considerably with operating pressure, construction, and type of operation of the boiler. Although the makeup water may be subjected to a considerable amount of treatment before entering the boiler, water quality requirements are usually expressed in terms of the water within the boiler itself. Some quality requirements for the makeup water are almost self-apparent. It should certainly be free of any suspended matter. For those cases requiring low dissolved oxygen in the boiler, as much of this as possible should be removed before the water enters the boiler.

Heating boilers in which almost 100 per cent of the steam returns as condensate generally require protection only from corrosion, but regular checking is necessary to ensure against development of excessive accumulation of dissolved solids which might lead to scale formation. With chromate-treated boilers, water-treatment standards range from 500 ppm sodium chromate, which provides ample protection under conditions of good control, to 2,000 ppm sodium chromate as recommended for general use by the Steel Boiler Institute. With borate-buffered sodium nitrite as the corrosion inhibitor, a minimum of 2,000 ppm sodium nitrite is generally preferred.

Turning to process-steam boilers—those for which some regular makeup-water requirement is anticipated—Table 16-1 summarizes some typical recommendations for boiler-water composition at various operating steam pressures. Quite probably it would be impossible to obtain unanimous agreement on these water quality requirements from any substantial group of industrial water chemists, but they can serve as a general guide.

The divisions into various pressure classifications are arbitrary. Some of the quality specifications pertain particularly to certain types of construction for systems with certain auxiliary equipment, such as turbines. For each range of concentration given in Table 16-1, it is generally preferable to approach the lower limit as the boiler operating pressure approaches the upper limit of the pressure range.

Again, keep in mind that a table is no substitute for a competent boiler-water specialist. Many situations call for modification of the figures given in Table 16-1. For example, in the very high pressure range, in addition to the usual thermal circulation boilers, both forced circulation boilers and once-through boilers are used. For both of these, boiler-water requirements differ from those given in Table 16-1 for the same operating pressures. Thus, in a once-through boiler which evaporates the water almost completely in a single passage, total solids in the feedwater should be no higher than 0.5 ppm, and the pH should be in the range 8.8 to 9.2.

Another example of the flexibility of the figures in this table may be seen from a consideration of the maximum total-dissolved-solids limit. Generally speaking, this limit is for the purpose of minimizing foaming and priming. Few boilers are more susceptible to carrying over slugs of water as a result of foaming or priming than are the fast-disappearing railroad steam-locomotive boilers. Yet experiments have shown that when such boilers are fed with completely softened water containing a minimum of suspended solids, the dissolved solids content can safely be carried above 10,000 ppm with no significant foaming or priming. Therefore, it is well to keep in mind that the various boiler-water quality recommendations are designed for reasonably safe operation, but are not rigid limits.

HEATING WATERS

Quality requirements for water in closed recirculating heating systems are fairly simple. In all cases it is desirable to avoid suspended solids in order to minimize damage to pumps and other mechanical equipment. If the systems were truly tight, this is all that would be required. However, experience and chemical tracer studies have shown that completely tight systems are in the minority. One tracer study of 84 systems showed that the average water loss per month equaled the system volume.[2] A monthly loss of more than 10 system volumes has been observed.

In the usual low-pressure hot-water heating system, as in steam-heating

TABLE 16-1 Boiler Water Quality Recommendations at Increasing Pressures (All values except pH are given in ppm)

Constituent	Low, to 250 psi	Intermediate			High						Very high			Super-critical, over 3,000 psi
		250–300 psi	300–450 psi	450–500 psi	500–600 psi	600–750 psi	750–900 psi	900–1,000 psi	1,000–1,250 psi	1,250–1,500 psi	1,500–2,000 psi	2,000–2,500 psi	2,500–3,000 psi	
Total hardness, as $CaCO_3$	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Total alkalinity, as $CaCO_3$	....	700†	......	500†	500†	400†	300†	250	200†	200†	150†	100†	100†	
Hydroxide, as $CaCO_3$	150–300	......	130	100	100	100	100	50–75	50–75	50–75				
Silica,‡ as SiO_2	100–133	50–67	50–67	50–67	19–25	19–25	7.5–10	7.5–10	3.8–5	2.1–2.9	0.8–1.1	0.3–0.5	0.09–0.13	0.02
Dissolved oxygen, as O	0.015	......	......	0.007	....	....	....	....	....	....	....	......	....	0.005
Solids, dissolved	3,000–5,000	3,500†	3,000	2,500†	2,500†	2,000†	1,500†	1,250†	1,000†	1,000†	750†	500†	500†	0.05–0.5‡
Solids, suspended	300–600	300†	......	150†	150†	100†	60†	40†	20†	20†				
pH*	9.5	......	......	9.7	....	....	....	....	10.3–10.8	10.3–10.8	10.3–10.8	......	....	9.0–9.6
Oil	1.0	......	......	0.1										
Iron, as Fe	....	......	......	....	....	....	....	....	....	....	....	......	....	0.01‡
Copper, as Cu	....	......	......	....	....	....	....	....	....	....	....	......	....	0.01‡
Sodium sulfite,* as Na_2SO_3	30–60													
Phosphate,* as PO_4	40–80	30–50	30–50	20–40	20–40	20–40	20–40	20–40	20–40	20–40	20–40			
Organic dispersant*	50–75													

*These values minima. All others maxima.

†American Boiler Manufacturers Association recommendation.

‡Values are for feedwater, not boiler water. For silica, this applies to pressures over 500 psi.

boilers, corrosion, the major operating problem, can be minimized by maintaining a minimum of 500 ppm sodium chromate with good treatment control or 2,000 ppm sodium chromate as recommended for general application by the Steel Boiler Institute. Borate-buffered sodium nitrite at 2,500 ppm minimum is sometimes used as a colorless alternative.

Although corrosion control by the addition of sodium sulfite is not reliable for low-pressure steam-heating boilers because of the amount of oxygen that may be picked up by the condensate returned to the boiler, these conditions do not apply in hot-water heating systems, so that corrosion can also be minimized by maintaining a minimum of 50 to 100 ppm of sodium sulfite in the circulating water. With this type of treatment, periodic control analyses are required.

As the operating pressures of closed heating systems increase to the range of high-temperature hot-water systems (250 psi), a completely softened and deaerated water becomes necessary for makeup. The circulating-water pH is generally adjusted to a minimum of 9.5, and a sodium sulfite residual of 50 to 100 ppm may be maintained, together with a phosphate residual of 30 to 60 ppm.

For closed water loops used in nuclear installations, the development of radioactive impurities from either dissolved or suspended materials must be minimized. In these systems, the total dissolved solids and total suspended solids are kept to the lowest possible value in the circulating water by using deionized water as makeup and by passing the circulating water through a mixed-bed deionizer which reduces both suspended and dissolved solids.

TREATMENT METHODS

Inasmuch as most treatment methods are applicable to waters used for a variety of purposes, the presentation of treatment methods in this section will be related to the effects of the treatment upon water composition rather than to the end use of the water. Once again, it is important to emphasize that there is no single treatment method which is the "best" for achieving a given objective or change in water composition. The entire picture for any given case must be considered before making a selection of treatment method.

It is also appropriate at this point to call attention to the need for knowledge and caution in the treatment of industrial waters because of two potential hazards which are almost always present: the dangers to unskilled maintenance personnel of handling caustic, acidic, or toxic treatment chemicals; and the hazards of cross connections which can allow nonpotable treated waters to enter drinking-water systems.

Removal of Suspended Solids and Colloids

The familiar processes of sedimentation, coagulation, and filtration are often not needed for treatment of industrial waters. On the one hand, many installations of this type take water from public supplies, thereby receiving water which is already substantially free from suspended and colloidal materials. At the other extreme some consumers use such tremendous volumes of water for once-through cooling that they could not afford such treatment. Between these extremes there are many industrial plants and power stations which utilize surface supplies from which suspended and colloidal impurities must be removed before use.

Sedimentation, coagulation, and filtration are carried out industrially in substantially the same way as in municipal water-treatment plants. The higher value of water to industrial users makes for more common utilization of coagulant aids and certain auxiliary equipment, such as pressure filters, automatic backwash gravity filters, industrial strainers, and surface washers for filters. Filters which operate at flow rates above 2 gpm per square foot are more common in industrial practice than in municipal practice. These may employ larger sizes of sand or anthracite coal or combined sand and anthracite filter beds.

When cooling towers scrub from the air so much solid material that it would build up excessively in the circulating cooling water, the suspended solids may be limited to an acceptable level by passing some 3 to 5 per cent of the total circulation through a filter called a "side stream filter." Similar filters are sometimes used for lower-pressure process boilers to aid in limiting accumulation of precipitates formed by internal treatment of the boiler water for scale control.

Another industrial filtration removes colloidally dispersed oily material, such as traces of engine lubricants, from returned steam condensate prior to reusing it for boiler feedwater. The condensate is filtered hot, and because dissolved silica in the makeup for higher pressure boilers must be minimized, the filtering medium is always cloth or anthracite coal. A mixture of alum and alkali may be added to the oily condensate so as to create a layer of preformed alum floc on the filter medium, much as is done in recirculating swimming-pool filters. During backwash, it is important that the somewhat adherent oil-contaminated floc be thoroughly removed from the anthracite coal particles. To do this, oil removal filters may be equipped with rotary rakes to provide for better breakup of the filter bed.

Removal of Dissolved Solids

Prevention of scale and other deposits in cooling and boiler waters is best accomplished by removal of dissolved solids. Whereas in municipal water purification such removal is ordinarily limited to the partial reduction of hardness and the removal of iron and manganese, in industrial water treatment it is often carried much further and may include complete removal of hardness, reduction or removal of alkalinity, removal of silica, or even the complete removal of all dissolved solids (deionization or demineralization).

Treatment methods substantially the same as those used in municipal practice are employed for cold lime-soda softening, for zeolite (ion-exchange) softening, and for removal of iron and manganese. Because completely softened water is frequently required for steam generation, ion-exchange processes are widely used. The use of pressure softeners is far more common in industrial plants than in municipal water treatment.

When the water must be heated, as for boiler feedwater, advantage may be taken of the reduced solubility of calcium carbonate at higher temperatures by using hot-precipitation methods of softening. These are two-stage processes based upon hot lime precipitation of the bulk of the calcium and magnesium [Eqs. (1), (2), and (3)] followed by one of three alternate processes to further reduce the residual hardness of the water.

Hot Lime–Soda Softening. The first of these alternates is the old and well-known use of soda ash for removing most of the noncarbonate hardness [Eq. (4)].

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3\downarrow + 2H_2O \qquad (1)$$

$$Mg(HCO_3)_2 + Ca(OH)_2 \rightarrow Mg(OH_2)\downarrow + Ca(HCO_3)_2 \qquad (2)$$

$$MgSO_4 + Ca(OH)_2 \rightarrow Mg(OH)_2\downarrow + CaSO_4 \qquad (3)$$

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3\downarrow + Na_2SO_4 \qquad (4)$$

Hot Lime–Phosphate. The second alternate process is the addition of phosphate in the hot lime–phosphate procedure, shown in Eq. (5), where Eqs. (1), (2), and (3) apply. In addition to producing a much softer effluent because of the lower solubility of calcium phosphate, this treatment method offers some flexibility in adjusting the alkalinity of the treated boiler feedwater because the phosphate can be supplied as trisodium, disodium, or monosodium phosphate, or even as phosphoric acid.

$$3CaSO_4 + 2Na_3PO_4 \rightarrow Ca_3(PO_4)_2\downarrow + 3Na_2SO_4 \qquad (5)$$

The equipment in which hot lime and related softening processes are carried out, while similar in principle to that used for cold lime softening, differs in structure. Because of the higher temperatures used the equipment operates under pressure. If often includes deaeration and treated-water storage sections.

Hot Lime–Zeolite. In recent years the development of cation-exchange resins which are stable in high-pH water and at high temperatures has provided an additional working tool for removing the last traces of hardness left by the hot lime process. The hot lime–zeolite process, shown in Eqs. (6) and (7) has a number of advantages but requires special wash and regeneration procedures to avoid damage to the beads of ion exchange resin. Here again, Eqs. (1), (2), and (3) apply.

$$CaSO_4 + Na_2Z \xrightarrow{\text{softening}} CaZ\downarrow + Na_2SO_4 \tag{6}$$

$$CaZ + NaCl \xrightarrow{\text{regeneration}} CaCl_2 + Na_2Z \tag{7}$$

Alkalinity Reduction by Salt-Acid Ion-exchange Process. Alkalinity reduction for boiler feedwaters can also be accomplished by techniques other than hot lime softening. As mentioned earlier, the feeding of phosphate for internal treatment can also be used for adjusting alkalinity by adding the more acidic phosphates, including phosphoric acid and the metaphosphates. Ion-exchange processes can also be employed for reduction of alkalinity in the cold process. The oldest of these processes is the salt-acid procedure, in which part of the water is softened in the conventional salt-regenerated cation exchanger while another part is passed through an acid-regenerated cation exchanger which both removes all cations and converts the alkalinity to free carbon dioxide, as shown in Eqs. (8), (9), and (10). The latter can, of course, be readily removed by degasification.

$$Ca(HCO_3)_2 + Na_2Z \rightarrow CaZ\downarrow + 2NaHCO_3 \tag{8}$$

$$Ca(HCO_3)_2 + H_2Z \rightarrow CaZ\downarrow + 2H_2O + 2CO_2 \tag{9}$$

$$CaSO_4 + H_2Z \rightarrow CaZ\downarrow + H_2SO_4 \tag{10}$$

The proportion of water passing through each type of exchanger may be adjusted in accordance with the raw-water composition and the needs of the treated water so as to produce, upon blending, the desired composition of treated water which is both completely softened and reduced in alkalinity and total solids. This is in contrast to the usual sodium-cycle ion-exchange softening of water in which, because of the fact that sodium has a higher equivalent weight than calcium, there is an *increase* in total dissolved solids of the treated water. Table 16-2 compares the results produced by these ion-exchange processes on a single raw water.

Sodium and Anion-exchange Treatment. Another ion-exchange procedure both softens and reduces alkalinity by means of successive beds of cation-exchange resin and of strongly basic anion-exchange resin. The hardness of water passed through them is replaced by sodium, and the alkalinity and sulfate are replaced by chloride, as shown in Eqs. (8) and (11). Regeneration is effected by means of a salt solution, with that for the anion-exchange resin made slightly alkaline with caustic soda. This process finds most of its application in smaller installations.

$$Ca(HCO_3)_2 + Na_2Z \rightarrow CaZ\downarrow + 2NaHCO_3 \qquad (8)$$

$$NaHCO_3 + A.Cl \rightarrow A.HCO_3\downarrow + NaCl \qquad (11)$$

Scale in large evaporative cooling-water systems is commonly minimized by addition of sulfuric acid to reduce alkalinity. This is less expensive than complete softening but usually requires the installation of automatic pH control equipment in order to control the acid feed rate and maintain pH conditions which will not cause excessive corrosion. In addition, the equipment must be designed so that the concentrated acid is gradually mixed with the makeup water under conditions which will avoid the entry of low-pH water into the circulating water piping.

Deionization. Water for steam generation at higher pressures requires the almost complete elimination of dissolved solids. In the past, this could only be attained by distillation and, indeed, on shipboard and in many large power stations this is still the practice. The development of the ion-exchange process known as "deionization" or "demineralization" has provided an alternate procedure which does not require the heating of the water and, in most cases, is more economical than distillation.

In deionization the influent water cations are exchanged for hydrogen ions on an acid-regenerated cation-exchange resin, as shown in Eqs. (9) and (10), and the anions are exchanged for hydroxyl ions on an alkali-regenerated anion-exchange resin, as shown in Eqs. (12) and (13), leaving only water. This is an oversimplified statement of the process. A number of variations are possible according to the types of resins used, nature of the equipment, and the results desired. Weakly basic anion exchangers, for example, will remove neither carbon dioxide nor silica from water. The for-

TABLE 16–2 Changes Produced by Sodium and Hydrogen Cycle Treatment (All values in ppm as $CaCO_3$ except pH, CO_2, and total dissolved solids)

Constituent	Raw water	Sodium cycle effluent	Hydrogen cycle effluent	Blend: 29% sodium,—71% Hydrogen	
				Before degasification	After degasification
Cations					
Calcium	140	1	1	1	1
Magnesium	35	1	1	1	1
Sodium	20	193	2	58	58
Hydrogen	0	0	41	0	0
Anions					
Bicarbonate	150	150	0	15	15
Chloride	20	20	20	20	20
Sulfate	25	25	25	25	25
Other					
pH	7.5	7.5	3.0	5.3	6.6
Carbon dioxide (free)	10	10	142	129	10
Total dissolved solids	202	311	40	83	83

mer may be removed by degasification, and the latter is inoffensive in many processes requiring deionized water. At the other extreme, the use of a strongly basic anion exchanger in a mixed bed of cation and anion exchangers will produce a deionized water which is completely free of carbon dioxide and silica and as close an approach to conductivity water as it is possible to obtain by any large-scale process.

Cation-exchange stage:

$$Ca(HCO_3)_2 + H_2Z \rightarrow CaZ\downarrow + 2H_2O + 2CO_2 \qquad (9)$$

$$CaSO_4 + H_2Z \rightarrow CaZ\downarrow + H_2SO_4 \qquad (10)$$

Anion-exchange stage:

$$CO_2 + A.OH \rightarrow A.HCO_3\downarrow$$

$$H_2SO_4 + A.OH \rightarrow A.HSO_4\downarrow + H_2O \qquad (13)$$

When selecting water treatment for a power plant, the choice between distillation and deionization can be made only after a rather complex study of many factors, including the economics of the heat balance for the particular plant. The two processes are combined at times, utilizing deionization as an initial stage and distillation as a second stage in order to obtain optimum water quality and economy.

The degree of removal of dissolved solids by present deionization equipment can be truly remarkable. A two-stage ion-exchange procedure in which the water first passes through separate cation and anion exchangers and is then "polished" by passage through a mixed-bed cation-anion exchanger produces a water with conductivity of only 0.1 μmho per centimeter (10 million ohm resistance), corresponding to less than 0.1 ppm of dissolved solids, including less than 0.01 ppm of silica.

Precipitation of potential scale formers within the boiler itself (internal treatment) is the most common procedure for removing certain dissolved solids in low-pressure- and medium-pressure-process boilers. By addition of appropriate treatment chemicals the precipitated calcium and magnesium can be kept suspended as a nonadherent "fluid" sludge, which can be removed from the boiler by intermittent or continuous blowdown as described below.

Internal boiler-water treatment chemicals are frequently classed as "boiler compounds." This terminology is used for mixtures which range from proprietary products of little or no value to mixtures of standard chemicals carefully formulated for particular water composition and boiler operating conditions.

The basis of most effective boiler-water treatment formulations is threefold: (1) an alkali—this may be soda ash, caustic soda, or an alkaline phosphate which plays a twofold role in the mixture; it supplements the alkalinity of the makeup water to cause the precipitation of most of the hardness as calcium carbonate and magnesium hydroxide; (2) a phosphate, which serves to precipitate the last traces of calcium; and (3) an organic dispersant to keep the sludge "fluid" for easy disposal by blowdown; this may be quebracho or other tannin, alginates, lignin sulfonates or other natural or synthetic products, some of which are alleged to have supplementary properties, such as removal of dissolved oxygen.

Internal treatment of boiler waters may also include additional chemicals for other purposes. Among the more usual of these are sodium sulfite or hydrazine for oxygen removal, volatile or filming amines for condensate-line corrosion control, and various organic compounds having antifoam properties for control of priming and foaming.

In many evaporative systems, both for cooling waters and for boiler waters, total dissolved and suspended solids must be maintained lower than a predetermined maximum, although they need not be completely removed. In order to do this, a portion of the body of water is discharged to waste continuously or intermittently. This bleed or bleedoff in the case of cooling waters and blowoff or blowdown in the case of boiler waters effectively limits suspended, as well as dissolved, solids. The amount or rate of bleed or blowdown required for maintaining a given maximum solids limit can be calculated from a materials balance on the dissolved solids of the makeup and process waters. Although intermittent bleed or blowdown may be used, continuous bleed or blowdown permits so much better control of the dissolved-solids level that it is used wherever possible.

Silica from boiler water can dissolve in very high-pressure steam and then precipitate at lower pressures, forming difficult-to-remove deposits on turbine blades, thereby reducing power generation efficiency. The previous section pointed out that silica can be removed from boiler feedwater if strongly basic anion-exchange resins are used for deionizing. Several other procedures are also available for reduction or elimination of dissolved silica. The addition of magnesium salts or of dolomitic (high-magnesium) lime during cold- or, preferably, hot-lime softening reduces the silica content of the water.

Early Ion-exchange Silica-removal Process. Prior to the time when strongly basic anion exchangers became available, silica removal by ion exchange required the addition of sodium fluoride to the influent to a two-stage deionizer. Hydrofluoric acid formed during passage through the acid-regenerated cation exchanger and combined with the dissolved silica to form the fluosilicate ion, as shown in Eqs. (15) and (16). This was then removed by the weakly basic anion exchanger, as shown in Eq. (17), by virtue of the fact that fluosilicic acid is much stronger than silicic acid.

$$2NaF + H_2Z \rightarrow Na_2Z\downarrow + 2HF \qquad (14)$$

$$Na_2SiO_3 + 6HF \rightarrow Na_2SiF_6 + 3H_2O \qquad (15)$$

$$Na_2SiF_6 + H_2Z \rightarrow Na_2Z\downarrow + H_2SiF_6 \qquad (16)$$

$$H_2SiF_6 + 2A.OH \rightarrow 2A.SiF_6\downarrow + 2H_2O \qquad (17)$$

Removal of Dissolved Gases

In municipal practice, a water may be aerated in order to remove hydrogen sulfide or to reduce an excessively high concentration of carbon dioxide. This is also done from time to time in industrial water-treatment practice.

However, more complete reduction of carbon dioxide is often necessary in heating or cooling waters. Certain processes described earlier, such as deionization, will also remove carbon dioxide. Additional processes available for this purpose include addition of alkali or passage through a so-called neutralizing filter in which the water is brought into contact with calcium carbonate (calcite) with which the carbon dioxide reacts according to Eq. (18).

$$CO_2 + CaCO_3 + H_2O \rightarrow Ca(HCO_3)_2 \qquad (18)$$

The removal of another dissolved gas, oxygen, in order to minimize corrosion is one of the most important processes in the preparation of boiler feedwater. Both mechanical and chemical methods are available for this purpose. Mechanically, the oxygen can be removed by means of a vacuum deaerator at lower temperatures or by means of a deaerating heater at higher temperatures. In both cases the process is based on Henry's law: At any temperature the concentration of gas dissolved in the water is proportional to its partial pressure in the gas above water. From this, it becomes obvious that both vacuum and thermal deaerators will remove carbon dioxide and other gases as well as oxygen.

Chemical methods for removal of oxygen from water include reaction with sodium sulfite or with hydrazine. At low temperatures the reaction rate with sulfite is quite slow, but it can be accelerated by the addition of catalytic amounts of cobalt salts or copper salts, the former being more effective. The use of hydrazine as a scavenger for the last traces of oxygen in higher-pressure boilers is increasing but requires extremely close control. The reaction with oxygen appears to be slower than that of sodium sulfite, and side reactions lead in some cases to the formation of undesirable amounts of ammonia. However, the volatility of both hydrazine and its reaction products offers a distinct advantage in extremely high-pressure boilers.

Control of Dissolved Solids and Gases

The removal of some or all dissolved gases or solids has been discussed as a means of controlling scale and corrosion, but a satisfactory degree of control may often be obtained by alternate procedures without actual removal. Familiar examples of such processes in municipal practice are the addition of a few parts per million of polyphosphate in threshold treatment for preventing precipitation of scale in hard or lime-softened waters or for avoiding red water formation in corrosive waters, and the use of similar small amounts of polyphosphate or of silicates in order to delay the precipitation of iron from iron-bearing waters. These same processes are also used industrially.

There are additional methods for limiting the undesirable effects of dissolved solids and gases without removing them. Two such methods for controlling scale in industrial water supplies are limitation of the total solids, in order to prevent precipitation, and dispersion or sequestering, so that scale formation cannot occur even with normally scale-forming concentrations present. The first of these procedures employs a continuous or periodic bleed or blowdown to limit total dissolved solids as discussed earlier.

The second procedure most commonly utilizes small concentrations of polyphosphates alone or together with various complex organic substances in order to prevent the growth of crystals of calcium carbonate or other scale-forming compounds. The tendency of polyphosphates to hydrolyze to normal phosphates makes them inapplicable for scale control by threshold treatment in boilers (although polyphosphates are frequently fed to boilers as a means of minimizing calcium phosphate precipitates in boiler feed lines and then making available for precipitation of calcium phosphate the normal phosphate formed by reversion of the polyphosphate within the boiler). Among the organic chemicals used for scale control are quebracho or other tannins, alginates, and various lignin sulfonate materials produced during paper manufacture. Certain synthetic polymers are also used.

More limited in application because of their higher cost are complex organic compounds which react chemically with the calcium and magnesium, tying them up in the form of soluble chelate compounds. Such compounds include EDTA (ethylene-diamine tetra-acetic acid) and its salts. Their use in water treatment is limited because it requires both stoichiometric amounts of these relatively expensive organic compounds and special precautions.

In cooling waters, maintenance of 2 to 5 ppm of polyphosphate, along with control of the total solids content of the circulating water by means of a bleed so as to maintain a Langelier index of about +1.0, is usually sufficient to maintain reasonably good control over the buildup of hardness deposits in the system. Scale control is frequently improved by further addition of one of the organic dispersants mentioned above. It should be pointed out, however, that in some cases it is possible to get undesirably large deposits of calcium carbonate or of calcium phosphate with such treatment. In contrast, it is also possible with some waters to add no polyphosphate or organics and to maintain conditions corresponding to a much higher Langelier index without encountering serious scale difficulties. This situation usually results from the presence in the makeup water of naturally occurring organic matter which acts as a dispersant.

Corrosion control in boiler and cooling waters can be effected, among other procedures, by maintaining a definite minimum concentration of certain corrosion inhibitors. An alkaline pH alone is rarely sufficiently effective as a corrosion-control mechanism. Although the same corrosion inhibitors may be used for both cooling and heating waters, the required concentrations differ because of the different temperatures involved. The nature and amount of the other materials dissolved in the water can also affect the minimum concentration of inhibitor required for satisfactory protection of the system. Thus, brines require a higher minimum inhibitor concentration than do cooling waters.

Without question the most effective and most universally applicable corrosion inhibitor is sodium chromate when maintained at a sufficiently high concentration and at a pH of above 7, although the degree of protection depends upon many factors: temperature; concentration of other salts, particularly chlorides, in the treated water; the degree of control with which the water treatment is handled; and other conditions which may tend to localize corrosion, including the presence of different metals in the system, crevices, suspended dirt, and the like. The minimum effective chromate concentration may range from 200 ppm sodium chromate, in an air-conditioning system being operated with good treatment control and no excessively high chlorides in the water, through 2,000 ppm sodium chromate, for steel-tubed heating boilers which may be laid up with no special precautions during the summer months and may operate with no regular treatment control, to 3,600 ppm, for sodium chloride brine in a refrigeration system.

Many condenser cooling waters are treated for corrosion control with one of several patented chemical mixtures which require a much lower concentration of sodium chromate in conjunction with other chemicals, such as sodium polyphosphates or zinc salts. These mixed inhibitors require less than 50 ppm of each component in the water, but are characterized by the need for close pH control, generally within the range 6.2 to 6.8, in order to achieve optimum effectiveness. The degree of protection afforded may be somewhat less than that attained with higher chromate concentrations alone. Using these procedures within the specified pH range, there is said to be less hazard of localized corrosion (pitting) should the inhibitor concentration fall too low. Although the statement that there is a distinct hazard of pit formation whenever chromate concentrations are low appears quite commonly in the corrosion literature, the experimental evidence indicates that the concentration must actually be below 25 ppm sodium chromate for this to occur.[5]

Unfortunately, the bright yellow color of chromate often makes its use objectionable because of the stains produced by leakage or drip from a treated system. One alternate inhibitor useful in both cooling and heating systems is sodium nitrite which, although colorless, is more restricted in its usefulness than is sodium chromate. It is generally necessary to maintain somewhat higher concentrations of sodium nitrite than of sodium chromate in order to obtain equivalent protection, and, in addition, such protection is provided only for steel. Sodium nitrite alone does not provide effective protection for cast iron and nonferrous metals. Indeed, it actually accelerates the corrosion rate of some metals, such as soft solder. A minimum pH of 7.0 is critical when nitrite is used. At lower pH it decomposes so that no inhibition is provided. In open systems biological oxidation at times rapidly converts nitrite to nitrate, which has no corrosion-inhibiting properties. In contrast to most other corrosion inhibitors, which become less effective as the chloride content of the treated water increases, nitrite becomes less effective as the sulfate content of the treated water increases.[6]

Nevertheless, despite these limitations, sodium nitrite is widely used as a corrosion inhibitor in cooling-water systems at minimum concentrations of about 500 ppm and in steel heating boilers at a minimum concentration of 1,500 to 2,000 ppm. For multimetal systems, such as hot-water heating systems with steel-tubed boilers and soldered copper-tubed convectors, sodium nitrite is the major constituent of a mixed inhibitor which contains, in addition to nitrite, borax as a pH buffer and an organic inhibitor, frequently mercaptobenzothiazole, for protection of copper and brass. This mixed inhibitor is used at a minimum concentration of about 2,500 ppm.

For corrosion control in moderate-pressure steam boilers, in addition to minimizing the dissolved oxygen and maintaining a 20- to 40-ppm residual of sodium sulfite, a minimum of about 200 ppm of caustic alkalinity is also recommended. As boiler operating pressures and temperatures climb, however, it becomes increasingly undesirable to have caustic alkalinity because of the increased possibility of caustic embrittlement at these higher pressures. Treatment procedures for minimizing such caustic attack have included the maintenance of specified control of the sulfate-carbonate ratio in the boiler water; the addition of tannin, lignin, and other organic compounds; the control of pH and phosphate in the boiler water so as to avoid the possibility of free caustic soda; and the addition of nitrates. This type of corrosion is really a variety of stress corrosion cracking.

The unbuffered nature of steam condensate makes it particularly susceptible to the development of highly corrosive conditions as a result of the absorption of very small amounts of carbon dioxide or of oxygen. Corrosion of condensate lines may be minimized by addition of volatile or filming amines to the boiler or to the steam. The former, usually morpholine or cyclohexylamine, distill over with the steam and maintain a sufficiently high pH in the condensate to minimize corrosion of return-line piping. Each of these amines has its own advantages. Cyclohexylamine has better volatility characteristics but can form deposits of cyclohexylamine bicarbonate in little-used lines or at closed valves.

The volatile amines become too costly when steam contains more than a few parts per million of carbon dioxide, and filming amines are then used. These are long chain organic amines, generally 16 to 18 carbons, often applied in the form of an emulsion of an acetate. They lay down a thin waxy film on the piping interior, thereby barring access to the metal by the water. Because of their detergentlike action, the start of filming amine treatment in an old system must be carefully controlled in order to minimize difficulties caused by dislodging of existing deposits of dirt and corrosion products.

Steam containing these volatile and filming amines may be used in contact with foods under certain restrictions. The Food and Drug Administration permits the use of steam containing morpholine up to 10 ppm and of steam containing filming amines up to 3 ppm except for processing of milk and milk products.

A summary of types of water treatment used with steam generators is given in Table 16-3. This is by no means complete and includes several different types of treatment for each problem. As indicated earlier, water treatment for any particular boiler must be selected only after complete consideration of all details of water composition, boiler construction, and operating conditions.

Control of Biological Organisms. Industrial water supplies, as well as municipal supplies, frequently require treatment for the control of other biological organisms, for example mollusks. The most common sterilization methods use chlorine and the many chlorine-yielding compounds for control of slime-forming bacteria and other organisms. Copper sulfate or proprietary copper salts compounded to keep the copper in solution are used for algae control. There are many industrial applications for which these treatment agents are objectionable. Thus, chlorine in excess of 1 ppm can cause deterioration of the wood in cooling towers, and traces of copper can cause intense localized corrosion in ferrous metal piping and other equipment.

Among the other bactericidal (more frequently known in industrial water treatment as "slimicidal") and algicidal chemicals used are chlorinated phenols, such as sodium pentachlorophenate, alone or in mixture with other chlorinated phenols; a variety of quaternary ammonium compounds; certain tin compounds, such as tributyl tin oxide; and many others. There are a considerable number of proprietary compounds offered for this purpose, most of which consist of members of the groups just mentioned, either alone or in various combinations.

Algae control can be simple in certain types of cooling equipment. A frequent location for heavy algae growths is in the head pan atop a large cooling tower. The construction of an opaque cover to prevent access of sunlight to this shallow pond of water often eliminates such growths. When algae grows in other locations accessible to light or when the construction of such a cover is not practical, chemicals of the types mentioned above are applied.

TABLE 16-3 Steam-Generator Water Treatment

		Types of water treatment used								
		Internal		External						
Problem	Location	Feed-water	Boiler water	Deaeration	Ion-exchange softening	Deionizing	Alkalinity reduction	Hot-process softening	Silica removal	Oil removal
Scale or deposit formation	Feedwater lines or heaters	×			×			×		×
	Economizer ...		×	×	×		×	×		
	Boiler drum and tubes		×		×	×		×	×	×
	Superheater ...		×			×		×	×	×
	Turbine blades					×		×	×	
Corrosion	Feedwater lines or heaters	×		×			×	×		
	Economizer ...			×			×	×		
	Boiler drum and tubes		×	×				×		
	Condensate lines		×	×			×	×		
Foaming and priming			×							×

Mollusks and similar marine growths can develop in once-through cooling systems utilizing seawater, estuarine waters, or river waters. The volumes of water handled in these systems are so large that continuous addition of sterilizing chemicals would be economically impossible. Accordingly, treatment generally consists of intermittent chlorination, e.g., ½ hr in every 6 or 12 hr or shutting off the water so as to permit temperatures to build up to the point at which the organisms are killed.

CONCLUSION

To persons familiar only with municipal water treatment, this chapter will have revealed that treatment of water for cooling, heating, and steam generation is more complex than is treatment of water for human consumption. In addition to the greater variety of treatment methods required by the greater variety of potential problems, the selection of a treatment method requires careful analysis of each individual case from the engineering and operational aspects, as well as from the chemical viewpoint.

This complexity has led to the offering for sale of a variety of "miracle" water conditioning gadgets which are usually characterized by broad claims to correct virtually all water-caused troubles with little or no attention after installation. Their performance is said to be based upon obscure electrical, catalytic, magnetic, radioactive, or other effects which, oddly enough, seem to have escaped the attention of the many competent chemists and engineers practicing in the field of water treatment. Theoretical calculations, laboratory tests, and careful investigations of field performance have consistently shown that these devices are not worth the paper on which their testimonial letters are written.[7,8]

Many treatment chemicals used for industrial waters are more hazardous to handle and are potentially more toxic than are most of the chemicals used in municipal water treatment. Unavoidably, particularly in smaller systems, it becomes necessary at times to place these chemicals in the hands of persons who are not trained in the safe handling of chemicals and to utilize them in systems which may present cross-connection hazards. Every precaution must be taken to anticipate and minimize the safety and public health hazards associated with industrial water-treatment processes.

These various considerations emphasize the importance of consulting a specialist experienced in industrial water treatment prior to establishing a program for the treatment of water in cooling, heating, or steam generating systems and of providing effective supervision and control of such programs during operation.

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17

Chemicals and Chemical Handling

By J. C. VAUGHN, G. J. TURRE, and B. L. GRIMES

LIST OF CHEMICALS USED IN WATER TREATMENT*

COAGULANTS AND COAGULANT AIDS

Coagulants

Aluminum sulfate (bauxite)
Ferrous sulfate
Ferric sulfate
Ferric chloride
Sodium aluminate
Hydrated lime and quicklime
(see "Softening")
Aluminum ammonium sulfate
Aluminum potassium sulfate

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*See Table 17-3 for detailed descriptions of the characteristics of these chemicals.

Coagulant Aids

Bentonite
Calcium carbonate
Carbon dioxide (see "Softening")
Sodium silicate
Organic coagulant aids as approved by Technical Advisory Committee on Coagulant Aids for Water Treatment (see text)

DISINFECTION AND DECHLORINATING AGENTS

Disinfection

Ammonia, anhydrous
Ammonium hydroxide
Ammonium sulfate
Bromine
Chlorine
Chlorine dioxide (sodium chlorite)
Chlorinated lime
Hypochlorites (calcium, lithium, and sodium)
Ozone
Silver

Dechlorinating Agents

Activated carbon
Aluminum ammonium sulfate
Ion-exchange resins
Sodium bisulfite (sodium pyrosulfite)
Sodium sulfite
Sulfur dioxide

HYDROGEN ION (pH) ADJUSTMENT

Calcium carbonate (see "Coagulant Aids")
Carbon dioxide (see "Softening")
Hydrochloric acid
Lime (quicklime and hydrated lime) see "Softening"
Sodium carbonate (see "Softening")
Sodium hydroxide
Sulfuric acid

FLUORIDATION AND FLUORIDE ADJUSTMENT

Fluoridation

Ammonium silico-fluoride
Fluospar (CaF)
Hydrofluoric acid
Hydrofluosilicic acid
Sodium fluoride
Sodium silico-fluoride

Fluoride Adjustment Agents

Activated alumina
"Fluo-Carb"
"Fluorex"
Ion-exchange resins
Magnesium oxide
Sodium bisulfate

TASTES AND ODORS

Activated carbon, powdered and granulated
Bentonite
Chlorine
Chlorine dioxide
Ozone
Potassium permanganate

MINERAL OXIDATION (IRON AND MANGANESE)

Chlorine
Chlorine dioxide
Ozone
Potassium permanganate

STABILIZATION AND CORROSION CONTROL

Quicklime and hydrated lime (see "Softening")
Sodium carbonate (see "Softening")
Sodium tri-polyphosphate
Sodium hexa-metaphosphate
Sodium hydroxide

SOFTENING

Carbon dioxide
Ion-exchange resins
Quicklime and hydrated lime
Sodium carbonate (soda ash)
Sodium chloride
Sulfuric acid (see pH-adjustment section)

MISCELLANEOUS

Copper sulfate
Sodium bichromate

COAGULANTS AND COAGULANT AIDS

Coagulants

Aluminum Sulfate. By far the principal coagulating agent is aluminum sulfate. Most commercial grades have the formula $Al_2(SO_4)_3 \cdot 14H_2O$. Aluminum sulfate is available in lump, ground, or liquid form, either purified or unpurified. The *lump* aluminum sulfate ranges in size from ½- to 3-in. particle dimensions. It is usually shipped in bulk (hopper cars or drums). It is sometimes used as a source material for preparing alum solution. An effective method of preparing this solution from lump alum is to dump the lump material into a bin and put it into solution by water sprays. The concentration of the resultant solution is measured, and it is fed through an appropriate feeding device for alum solution. Ground aluminum sulfate for use in dry-feed machines is available in either the purified or unpurified form. It should be of such size that not less than 90 per cent will pass NBS No. 10 sieve (9.21 openings per linear inch) and 100 per cent will pass NBS No. 4 sieve (4.22 openings per linear inch). It is a grayish-white crystallized solid completely soluble in water, with a tendency to absorb moisture from the air. Under such conditions it tends to deliquesce to a fine white powder. This does not affect its efficiency, except, to a slight degree in the weight fed. Ground aluminum sulfate may be shipped in 100-lb multiwall paper bags or in bulk in hopper railroad cars or trucks. The bulk material may be unloaded by devices of the pneumatic or bucket type. The fine material has a tendency to absorb moisture from the air and to stick to the sides of the unloading mechanisms. Some type of vibrator is necessary to loosen this caked material. The same property causes a tendency to "arch" in bulk-storage bins or in the hoppers of dry-feed machines. Vibrators are also used to correct this situation. (Care should be taken to avoid mixing dry aluminum sulfate with quicklime, as the water of crystallization from the alum will begin the slaking of the quicklime.) In enclosed containers, such as storage bins, the temperature is autocatalytic. At higher temperatures violent explosions are possible. Several such cases are on record. Ground alum is commonly fed in dry-feed machines of the semigravimetric or gravimetric type. The material is weighed at the desired rate into a solution tank where it is dissolved by the stirring action of propeller-type mixing. The solution tank is usually lead-lined, as the alum solution is slightly acidic. The alum solution is transmitted from the dry-feed machine to the point of application in rubber-lined or lead-lined pipes. Additional velocity through these lines is usually attained by the use of water eductors. The hazards associated with the use of dry alum are those usually connected with an acidic chemical dust. Protective clothing, neck cloths, gloves, goggles, and respirators should be provided for workmen wherever there is a danger of injury from the alum dust.

Liquid Aluminum Sulfate. This is a clear amber-colored liquid sometimes called "50 per cent" alum. This is because a gallon of liquid alum weighs approximately 10 lb and contains approximately 5 lb of dry aluminum sulfate. Actually it usually contains 8 per cent or more available water-soluble alumina (Al_2O_3), as compared with the 17 per cent available Al_2O_3 of the dry alum. Liquid alum may be shipped in tank trucks or railroad cars. The tanks should be rubber-lined or made of stainless steel (formula 316) or any other suitable material that will not be attacked by the acidity of the liquid (see Fig. 1). Tank-truck shipments are usually made to water plants within a 50-mile radius of the alum-producing plant. Tank-car shipments are made over the greater distances. In areas where the air temperature gets below 5 °F, the tank cars should be provided with insulation. Liquid alum may be stored in tanks that are lead- , plastic- , or rubber-lined. It may be transmitted through lines of similar material. Stainless steel may be used for such lines, but care must be taken to ensure that stainless steel of formula 316 is provided, as stainless steel of other formulas will not resist the action of the liquid alum. The alum liquid may be pumped by silicon-iron or other corrosion-resistant pumps. Liquid alum may be fed by an appropriate liquid chemical feeding device. A rotating volumetric device has been very satisfactory in many water plants. After measuring, the liquid alum may be transmitted to the point of application in the same type of lines indicated above. Dilution is sometimes used at this point, but runs the risk of causing precipitation of the insoluble material from the alum liquor. If the velocity is high enough, this material will be swept out of the line. Provisions for flushing lines should be provided. The hazards of using liquid alum are those common to an acidic solution. Protective clothing, gloves, goggles, face shields should be provided where

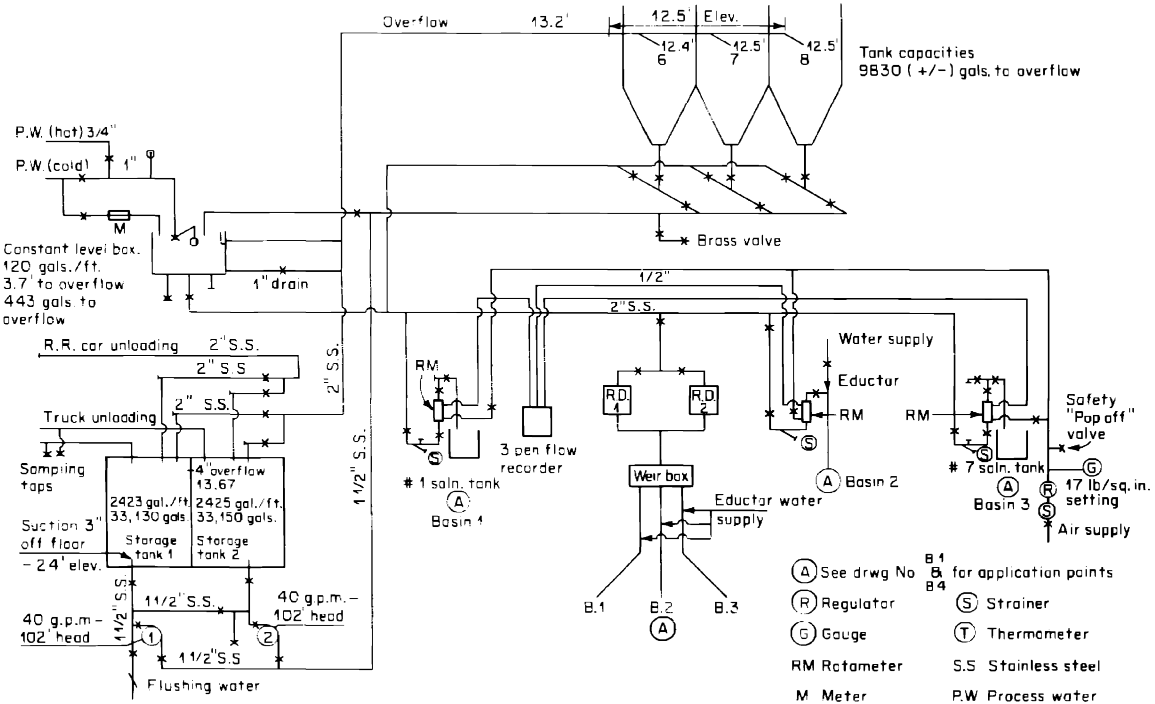


Fig. 1 Schematic drawing of alum solution system, South water filtration plant.

necessary. [For more details, alum users should consult the AWWA *Revised Standards for Aluminum Sulfate (Dry and Liquid),* AWWA Standard, B403-70.]

Bauxite. Bauxite is a mineral containing a preponderance of hydrated aluminum oxide. Its content varies considerably with respect to the aluminum oxide, iron, and silica. The AWWA Standard for Bauxite (B401-53T—discontinued) covers bauxite use in treating municipal and industrial water supplies. This standard calls for a silica content (SiO_2) not over 15 per cent. The total iron (Fe_2O_3) should not exceed 5 per cent. The aluminum oxide (Al_2O_3) should not be less than 55 per cent. (Some plants make their own aluminum sulfate by dissolving bauxite in sulfuric acid and applying the resultant solution directly to the water being treated. In a few plants a low-grade bauxite containing approximately 30 per cent Al_2O_3 has been used in this process. The end product is sometimes referred to as "Hoover" alum.) The material should be crushed so that no particle exceeds 2 in. in diameter. It may be shipped in bags or in bulk by available transportation equipment.

Ferrous Sulfate. The combination of ferrous sulfate and lime is an effective coagulant for the clarification of turbid water. Ferrous sulfate is also used for a base material for the preparation of chlorinated copperas. The ratio is 1 part chlorine to 8 parts ferrous sulfate as $FeSO_4 \cdot 7H_2O$. Ferrous sulfate is a greenish-white crystalline solid that is obtained as a by-product of other chemical processes, principally the pickling of steel wire or plate preparatory to galvanizing. The AWWA Standards of Ferrous Sulfate (AWWA B402-68) give size standards for both granular and lump ferrous sulfate. The standard-size granular ferrous sulfate has a tendency to cake and arch in dry-feeder hoppers or storage bins. Material may be obtained of a finer crystal size which also contains only 5 molecules of water crystallization ($FeSO_4 \cdot 5H_2O$). This shows less of a tendency toward caking or arching. Ferrous sulfate is also available in the liquid form. The spent pickle liquor, which is the source of most ferrous sulfate, is treated with scrap iron wire until the acidity is reduced to a very low point (0.02 per cent), and this material is supplied directly to the user. Since both dry and liquid ferrous sulfate are essentially by-products and may have been in contact with metal alloys, steps should be taken to ensure the absence of heavy metals. The heavy metals test as used in the revised AWWA Standard (B703-60T) should be applied to both forms of ferrous sulfate. The impurities (arsenic, antimony, and lead) would be grouped as "heavy metals." The "heavy metals" content would be limited to 0.031 per cent and would be determined by means of a revision of the method now suggested for "heavy metals" in the present AWWA Standard Specifications for Sodium Fluoride (B701-71). This revision would be made to read somewhat as follows:

Reagents: Same as listed in the sodium fluoride specification except that concentrated hydrochloric acid will not be needed.

Procedure: Dilute 2.0 g of sample to 40 ml with distilled water. Neutralize 20 ml of this solution with 10 per cent ammonium hydroxide. Add 1.0 ml of 0.10N hydrochloric acid and 10 ml of a freshly prepared saturated solution of hydrogen sulfide in distilled water. The brown color produced should not be greater than that exhibited by 0.31 mg of lead in an equal volume of distilled water containing the same quantities of reagents used in the test (0.31 mg lead is equivalent to 0.031 per cent heavy metals expressed as Pb).

The same type of materials and equipment that are used for dry and liquid aluminum sulfate may be used with dry and liquid ferrous sulfate in packing, shipping, storing, and feeding. The hazards of handling ferrous sulfate in all its forms are identical to those for alum.

Ferric Sulfate. Ferric sulfate, $Fe_2(SO_4)_3$, is produced to some degree when ferrous sulfate is chlorinated. (Ferric chloride is also one of the products of this reaction.) It is available on the chemical market as a reddish-brown deliquescent solid. It is shipped in asphalt-impregnated paper bags and has sometimes been shipped in ordinary steel railroad hopper cars in bulk. It has also been fed in the conventional type of dry-feed machine, but it was necessary to subject such equipment to frequent cleanings and protective coatings. Ferric sulfate is soluble in water producing a somewhat acidic solution. The acidic solution must then be transmitted to the point of application through corrosion-resistant lines. These lines should be provided with cleanouts so that the lines may be flushed periodically. Because of the extremely acidic nature of this material, the user must be more careful to provide more adequate protection than is necessary with alum or ferrous sulfate.

Ferric Chloride. Ferric chloride, $FeCl_3 \cdot 6H_2O$, is primarily used in the coagulation of sewage and industrial wastes. It is sometimes used in the coagulation of water. As mentioned above, it is one of the end products of the reaction produced by the chlorination of ferrous sulfate. Normally, it is produced by chlorinating scrap iron. It is now available in liquid form as a by-product, in certain areas. It is an orange-yellow, very deliquescent crystalline solid. It is highly soluble in water and in the presence of moist air or light decomposes to yield hydrochloric acid. It must be shipped, stored, and fed in equipment and devices that are corrosion-resistant. The hazards are those of a highly acidic chemical compound.

Sodium Aluminate. Sodium aluminate, $Na_2Al_2O_4$, is sometimes used as an auxiliary coagulant for the removal of fine turbidity and/or color bodies in soft, low-pH waters. The solid form is a white or brown powder containing 70 to 80 per cent $Na_2Al_2O_4$. The solution form is a concentrated solution containing approximately 32% $Na_2Al_2O_4$. (For further details, refer to

AWWA Standard B405-60.) This material is readily soluble in water producing a noncorrosive solution. It may be shipped, stored, and fed in devices that are standard in the waterworks industry.

Hydrated Lime and Quicklime. Lime, $Ca(OH)_2$, (CaO), is frequently used as a coagulant aid in waters that are high in magnesium compounds. This is because the magnesium hydroxide is precipitated by excess lime. This hydroxide has properties similar to iron and aluminum hydroxides. In softening plants where 20 to 30 ppm of excess lime are carried, the uses of other coagulants are often considered unnecessary. The properties and methods of handling lime will be treated more fully in the section on softening later in this chapter.

Aluminum Ammonium Sulfate. Aluminum ammonium sulfate, sometimes called "ammonium alum," $AlNH_4(SO_4)_2 \cdot 12H_2O$, is occasionally used as a water coagulant. Since it is a comparatively expensive material, its use is limited to small installations, such as swimming pools and boiler feed-water makeup tanks. It is sometimes produced in the shape of round balls which are placed in a container that is placed in the water line to the system receiving the treatment. The rate of solution is proportional to the rate of flow, but the control is otherwise somewhat empirical. It is a noncorrosive material and may be shipped in multiwall paper bags or drums.

Aluminum Potassium Sulfate. This material, $AlK(SO_4)_2 \cdot 12H_2O$, sometimes called "potash alum," exists in the form of white crystals with an astringent taste. Its properties and uses are similar to those described for ammonium alum. It is equally expensive, and its use in water treatment is limited to swimming pools and boiler feed waters.

Coagulant Aids

Bentonite. Bentonite, a form of clay that swells on absorbing moisture, is frequently used as a coagulant aid in waters of very low turbidity. It has a certain clarifying effect due to blanket entrainment if large quantities are used. A number of water plants around the shore of Lake Michigan use bentonite as a coagulant aid during periods of low turbidity. Several plants equipped with "up-flow" clarifiers use bentonite to help produce a heavy "sediment blanket." It is mined in areas of the United States ranging from the Gulf States to the Pacific Northwest. It may be shipped in burlap bags or in bulk by hopper railroad cars or trucks. It should be stored in a dry place and may be fed with the conventional dry-feed machine. There are no significant hazards in the handling of bentonite.

Calcium Carbonate. $CaCO_3$ is available in a number of forms, both prepared and occurring naturally. It is known as "whiting" or "precipitated chalk." When used as a coagulant aid, it is for the purpose of adding weight to aluminum or iron hydroxide flocs or providing a nucleus around which flocs can form. It is an inert material and only slightly soluble in water and may be handled in standard material-handling equipment. There is a slight dust hazard in handling this material.

Carbon Dioxide. The use of carbon dioxide, CO_2, as a coagulant aid is primarily for adjusting the pH or solubilities so that proper coagulation is obtained. (For further details, see section on softening.)

Sodium Silicate. Sodium silicate, Na_2SiO_3, known as "activated silica," is called a coagulant aid. The chief advantage of activated silica is its ability to toughen the flocs through ionic and electronic bond formation and thus form a cross-linking network which bridges larger particles and enmeshes those smaller (some authorities therefore consider it a coagulant). Activated silica is prepared in a number of ways. Sodium silicate solution is available as 40° Bé containing approximately 30% SiO_2. This material is shipped in ordinary tank cars, trucks, or drums and may be stored in ordinary steel tanks. To avoid "skin" formation it should be diluted approximately 40 per cent on storage. It may be activated by treating with various chemical reagents. Some of those agents that are in general use are chlorine, ammonium sulfate, aluminum sulfate, sulfuric acid, and carbon dioxide. One of the more common forms of activated silica is the "Baylis sol," prepared by using sulfuric acid. In this process the sodium silicate solution is diluted to approximately 1½% SiO_2. It is then treated with approximately 50 per cent sulfuric acid until the resultant total alkalinity of the solution is between 1,100 and 1,200 ppm. The solution is then aged for 2 hr. It is then diluted until the SiO_2 content is approximately 0.6 per cent. This final solution is then applied with aluminum sulfate. The proper ratio of aluminum sulfate to SiO_2 ranges from 8:1 up to 12:1. It is usually more effective in cold, clear waters.

Organic Coagulant Aids. These materials have come into wide use in the waterworks industry in the last decade. There has been created a USPHS Technical Advisory Committee on Coagulant Aids for Water Treatment. This committee has provided a list of those organic coagulant aids which it has indicated "may be used in water treatment without any adverse physiological effect on those using the water, when used in the concentration recommended by the manufacturer, and provided the product continues to meet the quality specifications furnished the committee."

The list follows:

Manufacturer	*Product*	*Maximum concentration recommended by manufacturer, ppm*
Allyn Chemical Co.	Claron	1.5
	Claron #207	2
North American Mogul Products Co.	Mogul CO-982 (identical to Claron)	1.5
	Mogul CO-980 (identical to Claron #207)	2

American Cyanamid Co.	Magnifloc 990	1
The Burtonite Co.	Burtonite #78	5
Dow Chemical Co.	Separan NP10 potable water grade Purifloc N17	1 1
North American Mogul Products Co.	Mogul CO-983 (identical to Separan NP10 potable water grade)	1
Dearborn Chemical Co.	Aquafloc 422 (identical to Separan NP10 potable water grade)	1
Key Chemicals, Inc.	Key-Floc-W (a 4% aqueous solution of Separan NP10 potable water grade)	25
Betz Laboratories, Inc.	Poly-Floc 4D (a 4% aqueous solution of Separan NP10 potable water grade)	25
Drew Chemical Co.	Drewfloc	1.8 alum 0.5:10 lime
Electric Chemical Co.	Ecco Suspension Catalyzer #146	3.5
Metalene Chemical Co.	Metalene Coagulant P-6	5

NOTE: The names of more recent approvals may be obtained by consulting the current waterworks literature.

DISINFECTION AND DECHLORINATING AGENTS

Disinfection

Anhydrous Ammonia. Various physical and chemical characteristics of anhydrous ammonia, a chemical compound, are summarized in Tables 17-1 and 17-2. In the gaseous state, ammonia is colorless and is about 0.6 times as heavy as air. The liquid, also colorless, is about 0.68 times as heavy as water. Unconfined liquid ammonia rapidly vaporizes to gas. The temperature-pressure-density characteristics of anhydrous ammonia are shown in Fig. 2.

Ammonia is a very reactive compound, forming ammonium salts with inorganic and organic acids and forming amines with halogens or with oxygen-containing compounds. Common metals are not affected by *dry* ammonia; *moist* ammonia, however, reacts with copper, brass, silver, zinc, and many alloys, especially those containing copper. Iron or steel is preferred for ammonia containers, fittings, and piping materials.

Ammonia gas is capable of forming explosive mixtures with air, but the explosive range is seldom encountered in practical handling. The explosive range is broadened by admixture of oxygen replacing air and at pressures and temperatures higher than atmospheric conditions. The presence of oil or the mixing of ammonia with other combustible materials increases the fire hazard.

Ammonia vapor is not poisonous, but due to its high solubility it has a very irritating action on the mucous membranes of the eyes, nose, throat, and lungs. Its sharp, pungent odor is readily detected at concentrations of about 50 ppm. It is unlikely that any person will remain in an atmosphere seriously contaminated with ammonia unless he is unconscious or trapped. Contact with the liquid causes severe burns.

The ACGIH (American Conference of Governmental Industrial Hygienists) has established the 8-hr, time-weighted (threshold limit) concentration at 100 ppm or approximately 70 mg per cubic meter. Prolonged exposure to air containing 100 ppm is not harmful, but breathing air containing 5,000 to 10,000 ppm may cause sudden death from spasm or inflammation of the larynx. Concentrations exceeding 700 ppm will cause eye irritation and permanent injury unless immediate remedial measures are taken (see Table 17-2).

Ammonia-gas feed equipment is similar to that used for chlorine, although different corrosion characteristics require the use of different construction materials. The high solubility of ammonia gas in water precludes the necessity of diffusion equipment, and dry gas is delivered from the control mechanism into the major flow of water to be treated through a small-diameter iron or steel pipe. Plastic lines are not satisfactory for ammonia unless they are impervious to water vapor. Other pertinent considerations are: the capacity of gas handling equipment is reduced by 50 per cent in comparison to chlorine because of the difference in density; over five times as much heat is required to vaporize ammonia as for chlorine; the injector water supply for solution-feed machines must be low in calcium hard-

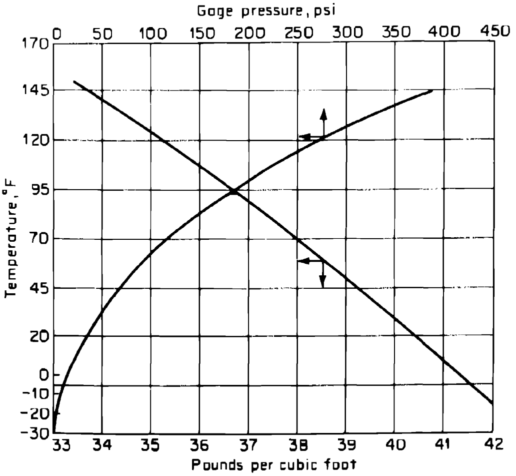
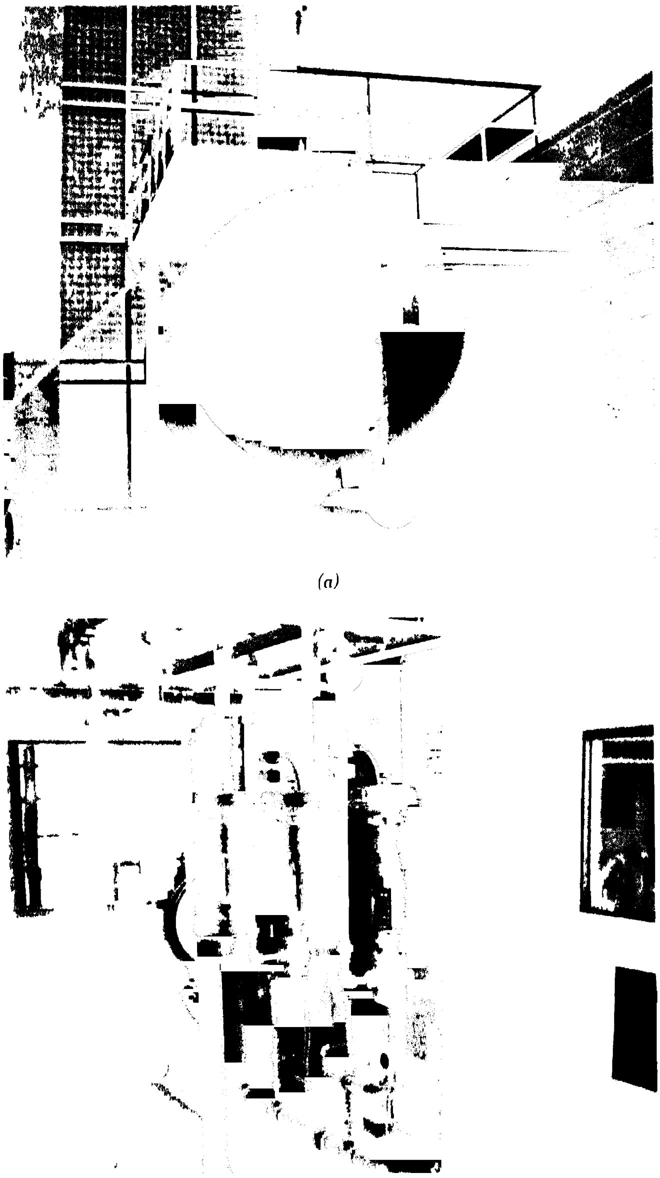


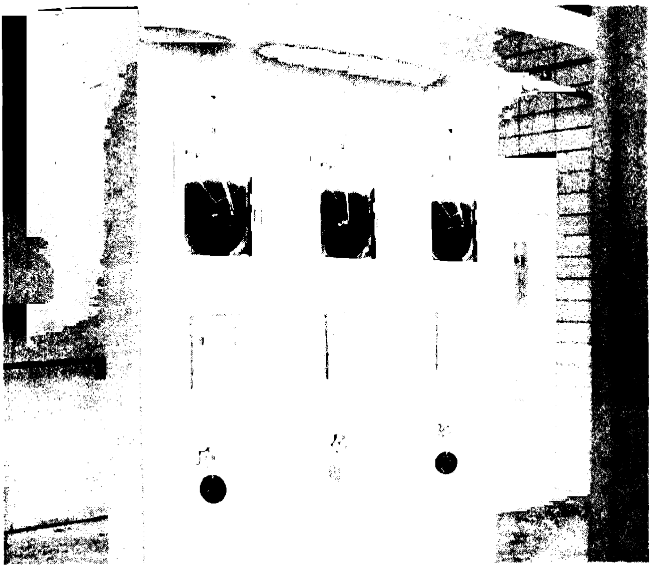
Fig. 2 Pressure-temperature and density-temperature curves of anhydrous ammonia.



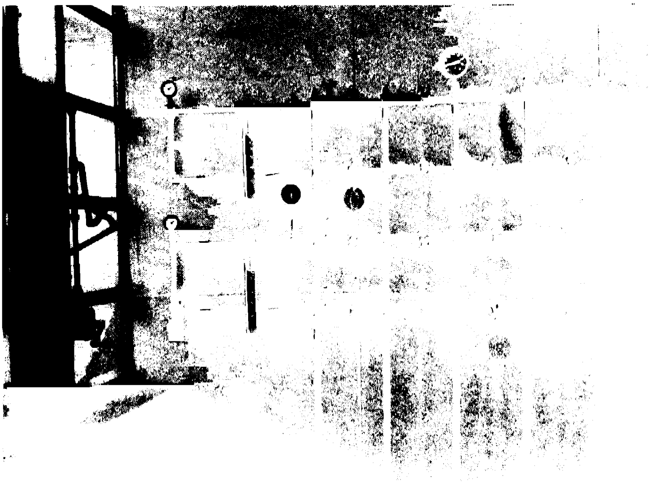
(a)

(b)

Fig. 3 Anhydrous ammonia system, South District filtration plant *(a)* Ammonia tank with heater, *(b)* feed regulators, *(c)* feed panel and charts, *(d)* distributor manifold



(c)



(d)

ness to prevent deposition of calcium carbonate in the solution line; and the solubility of ammonia in water, though relatively high, decreases as pH increases. For a typical application, see Fig. 3.

Ammonium Hydroxide. Anhydrous ammonia is quite soluble in water (considerably more so than either chlorine or sulfur dioxide), forming ammonium hydroxide. At 32 °F its solubility is about 90 per cent by weight; at 212 ° F, it is about 7 per cent. The practical advantages are observed in the use of dry-feed ammoniators for feeding ammonia gas and in the use of water sprays for controlling serious ammonia leaks. Aqua ammonia is the ammonium hydroxide of commerce. At 60 °F it consists of a stable solution of 29.4% NH_3, having a specific gravity of 0.8974, a density of 16.48 lb per cubic foot, and boiling and freezing points of 81 °F and —107 °F, respectively; its vapor pressure varies from about 4.5 psia at 32 °F to 50 psia at 104 °F. Because ammonia is readily soluble in water, fire sprinklers and water hoses are quite effective in removing ammonia gas from the atmosphere.

Aqua ammonia is quite volatile at atmospheric temperatures and pressures; the rate at which ammonia is given off is a function of the temperature of the surrounding atmospheric temperature and of the surface area of the ammonia liquor. Pressure does not develop in storage containers kept below 80 °F; above this temperature, the NH_3-H_2O equilibrium is upset, ammonia gas is evolved, and the solution is weakened if the container is opened. If the container is closed tightly, ammonia redissolves because of its vapor pressure, and a new equilibrium is established.

Aqueous solutions of ammonia exert a local irritating action; strong solutions cause tissue destruction on contact with eyes, skin, mucous membranes, gastrointestinal mucosa, or pulmonary tissue. The consequences of skin contact vary from a relatively mild dermatitis to severe burns, depending upon the strength of solution, length of contact, and individual sensitivity. Vaporization causes effects of the gas discussed above.

Ammonium Sulfate. Ammonium sulfate, $(NH_4)_2SO_4$, is used by many water plants as a source of ammonia in the formation of chloramines. It is a by-product of the coal and petroleum industries. It may vary widely in purity, and specifications should be very carefully written and should conform to AWWA Standard B302-64. Since it is a by-product material, it should be carefully examined for the presence of heavy metals. It is a white, crystalline solid that is readily soluble in water and may be fed in conventional dry-feed machines. It may be shipped in paper bags or in bulk in hopper cars or trucks. It has a tendency to cake, which may be helped by the addition of a small amount of clay (e.g., 1½ per cent) such as bentonite. The use of detergents as anticaking agents should be carefully avoided because of the possible effect of the detergent compounds on water quality. Ammonium sulfate solution may be transmitted through a reasonably corrosion-resistant piping. (Note that in the presence of chlorine where the chlorine-ammonia ratio is less than 10:1, chloramines are formed and the ammonia does not dechlorinate the water.)

Bromine. Bromine, Br_2, is a highly corrosive liquid. It is reddish-brown in color, has very irritating fumes, burns the skin, and is slightly soluble in water. It is sometimes used in the sterilization of water, but must be handled with great care. Corrosion-resistant equipment must be used throughout the process. It is not a very important factor in the purification of water.

Chlorine. Various physical and chemical characteristics of the element chlorine are summarized in Table 17-1. In the gaseous state, chlorine is greenish-yellow in color and is about 2.48 times as heavy as air; the liquid is amber-colored and is about 1.44 times as heavy as water. Unconfined liquid chlorine rapidly vaporizes to gas; one volume of liquid yields about 450 volumes of gas.

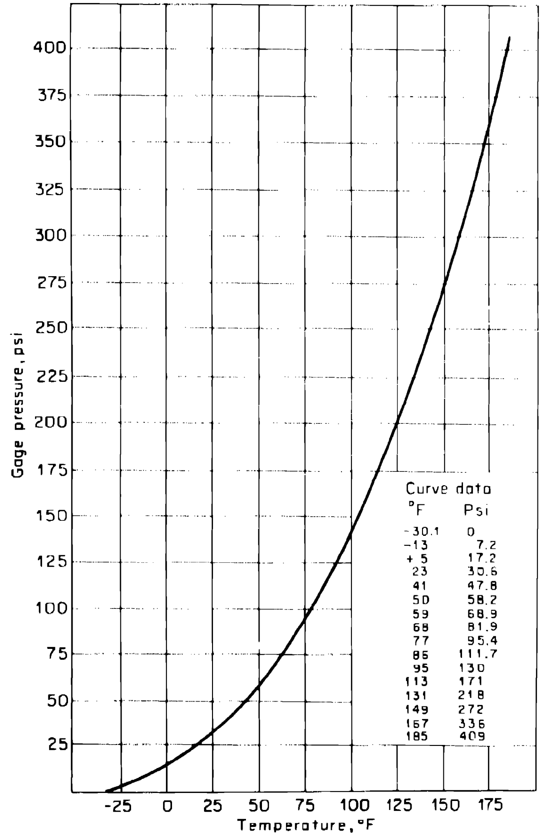
Chlorine is only slightly soluble in water, its maximum solubility being approximately 1 per cent at 49.2 °F. At temperatures below 49.2 °F, chlorine combines with water forming chlorine "ice," a crystalline hydrate ($Cl_2 \cdot 8H_2O$). When the water supplying a chlorinator is at a sufficiently low temperature to cool moist chlorine gas to the point at which chlorine ice

TABLE 17-1 Physical and Chemical Characteristics of Anhydrous Ammonia, Chlorine, and Sulfur Dioxide

Criterion	Anhydrous ammonia		Chlorine		Sulfur dioxide	
	Liquid	Gas	Liquid	Gas	Liquid	Gas
Formula	NH_3		Cl_2		SO_2	
Molecular weight	17.032		70.906		64.06	
Strength	About 99.5% NH_3		About 99.5% Cl_2		About 99.9% SO_2	
Affinity for water	Considerable	Considerable	Slight	Slight	Moderate	Moderate
Boiling point, at 1 atm	−33.35 °C (−28 °F)		−34.05 °C (−29.29 °F)		−10 °C (14 °F)	
Color	Colorless	Colorless	Clear amber	Greenish yellow	Water white	Colorless
Density, lb/cu ft	38.50 at 60 °F	0.04813 at 32 °F and 1 atm	88.79 at 60 °F	0.2003 at 32 °F and 1 atm	89.58 at 32 °F	0.1827 at 32 °F and 1 atm
Explosive limits in air, % by vol.		16–25	Non-explosive	Non-explosive	Non-explosive	Non-explosive
Flammability	Slight	Slight	Non-flammable	Non-flammable	Non-flammable	Non-flammable
Melting (freezing) point, at 1 atm	−77.7 °C (−107.9 °F)		−100.98 °C (−149.76 °F)		−75.5 °C (−103.9 °F)	
Odor	Suffocating, pungent	Same as liquid	Penetrating, irritating	Same as liquid	Suffocating, pungent	Same as liquid
Solubility, g/100 g H_2O at 20 °C and 1 atm		53.1		0.7293		
Specific gravity at 32 °F, compared to H_2O at 4 °C	0.639		1.468		1.436	11.28
Relative vapor density (air +1), at 32 °F and 1 atm		0.597		2.482		2.2638
Viscosity, centipoises	0.255 at −33.5 °C	0.00918 at 0 °C; 0.01279 at 100 °C	0.385 at 0 °C; 0.729 at −76.5 °C	0.01679 at 100 °C	0.4904 at −4 °F; 0.3923 at 32 °F; 0.2785 at 68 °F	0.0117 at 32 °F; 0.0145 at 68 °F; 0.0177 at 104 °F

is formed, accumulations on the needle valve and gas outlet tube develop, and erratic feed results. The condition can be corrected by warming that portion of the water which comes in contact with the chlorine or by slightly warming the chlorine-gas feed line. Because its vapor pressure increases with rising temperature, its solubility decreases with increasing temperature. At 212°F, it is insoluble in water; between 49.2°F and 212°F, chlorine dissolved in water forms a weak, corrosive mixture of hydrochloric and hypochlorous acids. Because of the limited solubility of chlorine, water is not a very satisfactory vehicle for disposing chlorine or for use in handling chlorine emergencies; moreover, the corrosivity of chlorine water creates additional problems in handling.

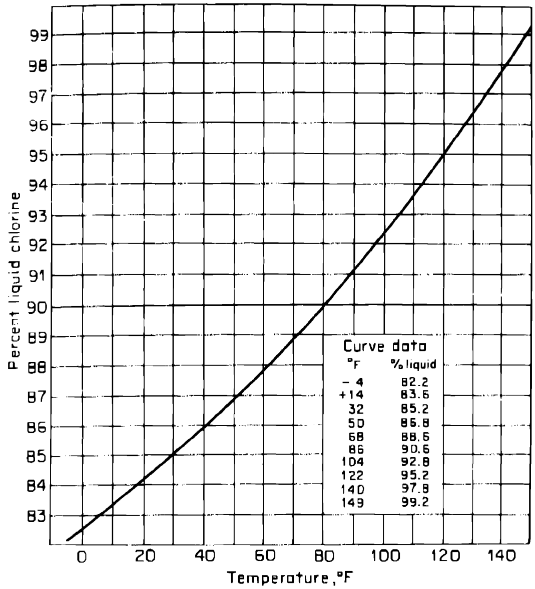
The temperature-pressure characteristics of chlorine are shown in Fig. 4. Chlorine confined in a container may exist as a gas, as liquid, or both.



Curve data

°F	Psi
-30.1	0
-13	7.2
+ 5	17.2
23	30.6
41	47.8
50	58.2
59	68.9
68	81.9
77	95.4
86	111.7
95	130
113	171
131	218
149	272
167	336
185	409

Fig. 4 Temperature-pressure curve, chlorine.



Curve data

°F	% liquid
- 4	82.2
+14	83.6
32	85.2
50	86.8
68	88.6
86	90.6
104	92.8
122	95.2
140	97.8
149	99.2

Fig. 5 Volume-temperature curve, chlorine.

Thus, any consideration of liquid chlorine includes that of gaseous chlorine. As will be noted, vapor pressure of chlorine in a container is a function of temperature and is independent of the contained volume of chlorine; therefore, gage pressure is *not* an indication of container contents.

The volume-temperature characteristics of chlorine in a container loaded to the limit authorized by Interstate Commerce Commission (ICC) regulations (as later discussed) are shown in Fig. 5. It is apparent that if a container is filled to this limit, it becomes completely liquid-full at approximately 154 °F; temperatures beyond that point may give rise to pressures that could result in hydrostatic rupture of the container. (Safety devices, as described in the appendix to this chapter, are provided to relieve excessive pressures accompanying dangerous temperature elevations.)

Under specific conditions chlorine reacts with most elements, sometimes with extreme rapidity. Because of its great affinity for hydrogen, chlorine removes hydrogen from some of its compounds, such as the reaction with H_2S to form hydrochloric acid and sulfur; it also reacts, as discussed later, with ammonia or nitrogen-containing compounds to form various mixtures of chloramines. It reacts much the same with organic materials to form chlorinated derivatives; some of these reactions can be explosive, including those with hydrocarbons, alcohols, and ethers. While neither explosive nor flammable, chlorine (like oxygen) is capable of supporting combustion of certain substances. It should, accordingly, be handled and stored away from other compressed gases (e.g., anhydrous ammonia), turpentine, ether, finely divided metals, and hydrocarbons or other flammable materials. Trichlorethylene and certain other chlorinated solvents, used in accord with the manufacturer's safety recommendations, are suitable for cleaning chlorine equipment; hydrocarbons or alcohols should not be used for this purpose.

Most common metals are not affected at normal temperatures by *dry* chlorine, either gas or liquid; below 230 °F, copper, iron, lead, nickel, platinum, silver, steel, and tantalum are resistant. *Dry* chlorine (gas or liquid) reacts with aluminum, arsenic, gold, mercury, selenium, tellurium, tin, and titanium and ignites carbon steel above about 450 °F. Antimony, arsenic, bismuth, boron, copper, iron, phosphorous, and certain of their alloys, in finely divided, powdered, or sponge form or wire in finely divided form ignite spontaneously in chlorine.

Moist chlorine is very corrosive to all common metals and reacts readily with mercury; gold, platinum, silver, and titanium are resistant. It can be handled in stoneware, concrete, glass, and porcelain equipment and by certain specialized alloys. Additionally, hard rubber, unplasticized polyvinyl chloride, Haveg, glass-fiber-reinforced Hetron resin, Saran, and Teflon have been used successfully. For higher pressures, combinations using resistant lining materials with the common metals for strength should be used.

Chlorine gas is primarily a respiratory irritant. Concentrations in air above 3 to 5 ppm by volume are readily detected by most persons. It causes varying degrees of irritation of the skin, mucous membranes, and the respiratory system, depending on the concentration and duration of exposure. In extreme cases death can occur from suffocation. The severely irritating effect of the gas makes it unlikely that any person will remain in a chlorine-contaminated atmosphere unless he is unconscious or trapped. Liquid chlorine may cause skin and eye burns upon contact with these tissues; when unconfined in a container, it rapidly vaporizes to gas producing the aforementioned effects.

The American Conference of Governmental Industrial Hygienists (ACGIH) has established the average 8-hr, time-weighted (threshold limit) concentration at 1 ppm or approximately 3 mg per cubic meter. Concentrations of 40 to 60 ppm for 30 to 60 min are dangerous, and concentrations of 1,000 ppm kill most animals in a very short time. (See Table 17-2.) Chlorine produces no known cumulative effects.

As noted, compressed gases of interest to waterworks management can be used either in the gas or liquid phase. Where natural heat transfer to a chlorine container or containers is insufficient to evaporate the chlorine at the desired rate without very complex manifolding systems, the chlorine must be withdrawn from the supply container or containers in the liquid

TABLE 17-2 **Physiological Response to Various Concentrations of Compressed Gases**

Effect	Ammonia,* ppm NH_3	Chlorine,† ppm Cl_2	Sulfur dioxide,‡ ppm SO_2
Least detectable odor	50	3.5	3-5
Max. amount that can be inhaled for up to 1 hr without serious disturbances	300-500	4	50-100
Noxiousness; impossible to breathe several minutes	....	5	150
Least amount required to cause irritation of throat	400	15.1	8-12
Least amount required to cause coughing	1,720	30.2	20
Least amount required to cause eye irritation	700	40-60	20
Amount dangerous in 30-60 min	2,500-4,500	1,000	400-500
Kills most animals in very short time	5,000-10,000		
ACGIH threshold limit	100	1	5

*CGA Pamphlet G-2 (Henderson & Haggard).
†Chlorine Institute "Manual" (Bur. Mines Tech. Paper 248).
‡CGA Pamphlet G-3 (various sources cited).

state and vaporized. Where requirements exceed about 2,000 to 3,000 lb per 24 hr, the use of an evaporator (vaporizer or heat exchanger) is usually required. Most proprietary equipment models, available in capacities up to about 8,000 lb per 24 hr maximum, include a sealed chlorine pressure chamber which is immersed in a hot-water bath vented to the atmosphere. The water is heated by electrical immersion heaters that are thermostatically controlled to maintain constant temperature and to ensure a superheated chlorine gas supply. Other models are steam-heated or heated with water piped to the unit.

Chlorine feeding equipment is designed to control and measure chlorine in the gaseous state and to apply it either as a gas or as an aqueous chlorine solution. Gaseous feed is predicated on these factors: the practice lends itself to accurate flow regulation, either manual or automatic; gas may be metered with variable-area or fixed-orifice-type flow meters (with or without recording instruments); and chlorine gas can be diffused into water.

Basically there are two distinct methods employed for applying chlorine gas: (1) direct feed, which involves metering of dry chlorine gas and conducting it under necessary pressure conditions to the water being chlorinated, and (2) solution feed, which involves metering of dry chlorine gas and dissolving it in the proper amount of water so that a relatively high-strength solution is applied to the water being chlorinated. In either case, the chlorine is dispensed to the feed equipment from an upright cylinder, the top (gas) outlet valve of a horizontal ton container, the gas valve of a single-unit tank car, the outlet of a chlorine evaporator, or a header valve in a chlorine gas piping system (see Fig. 6).

The practice of disposing chlorine gas from the source to the flow to be chlorinated without the use of either direct- or solution-feed methods is unsafe and should not be permitted.

Because chlorine gas is only slightly soluble in water (approximately 35 gal are required to dissolve 1 lb of gas at 68 °F), direct feed of chlorine gas under pressure into the water to be treated limits the rates at which gas can be fed. Undissolved chlorine in a moist environment presents corrosive conditions of serious magnitude. Direct-feed methods are required, however, where an operating water supply is not available. When direct-feed methods are employed, suitable means must be provided to ensure adequate diffusion of chlorine gas in the water flow being treated. Many difficulties have been encountered in the development of a diffuser that effectively disperses the chlorine and that at the same time will not be subject to clogging and frequent maintenance; at large installations direct feed might entail the use of a number of diffusers. In situations where low temperatures are encountered, the formation of chlorine ice might interfere with satisfactory operation. Because of these and other technical limitations and for safety reasons, the solution-feed method is by far the most common and preferred.

Equipment for the controlled application of chlorine gas can be categorized into two general types: (1) pressure feeders and (2) the more popular vacuum feeders.

Pressure feeders are equipped with a pressure-compensation valve which ensures gas metering accuracy regardless of pressure variations in chlorine containers (a function of temperature) and maintains a constant pressure drop across an orifice. The differential pressure drop across this orifice is measured and provides an indication of gas flow rate. (Certain equipment substitutes a volumetric hydraulic meter in which visible pulsations or bubbles of gas indicate flow rate.) Subsequently, the gas passes through a back-pressure regulating and check valve designed to maintain a constant downstream metering pressure and to prevent suck-back of liquid in the chlorine line in event of shutdown or due to the development of excessive back pressures at the point of application. Solution pressure feeders embody these same principles; however, they additionally include means, generally an injector, of introducing the metered gas into a minor flow of water which is applied at the desired point of chlorine application.

Vacuum-type solution feeders are a more recent development and embody radically different principles of operation. The chlorine gas enters the chlorine feeding equipment at some positive pressure, but is immediately reduced to a slight vacuum by a spring-loaded diaphragm-type reducing valve. The purpose of this is to maintain the chlorine gas at essentially a constant density for metering purposes. The gas then passes through a rotameter which indicates the rate of chlorine flow and guides the operator in making manual adjustments. The gas next passes through a variable-orifice type of meter and through another diaphragm-actuated differential valve, which functions to regulate the differential across the variable orifice. Control is accomplished by varying the area of the metering orifice, the differential across the metering orifice, or both. The chlorine gas then passes to a water-operated, aspirating type of injector or eductor in which gas may also be mixed with a small quantity of water preliminary to the point of application. The newer units also contain various devices incorporated primarily to protect the apparatus and operating personnel. The opening of the chlorine inlet valve is governed directly or indirectly by vacuum induced in the system. Thus, if the injector fails, if there is a break in the system, or if the discharge line becomes clogged, the chlorine feed is instantly stopped.

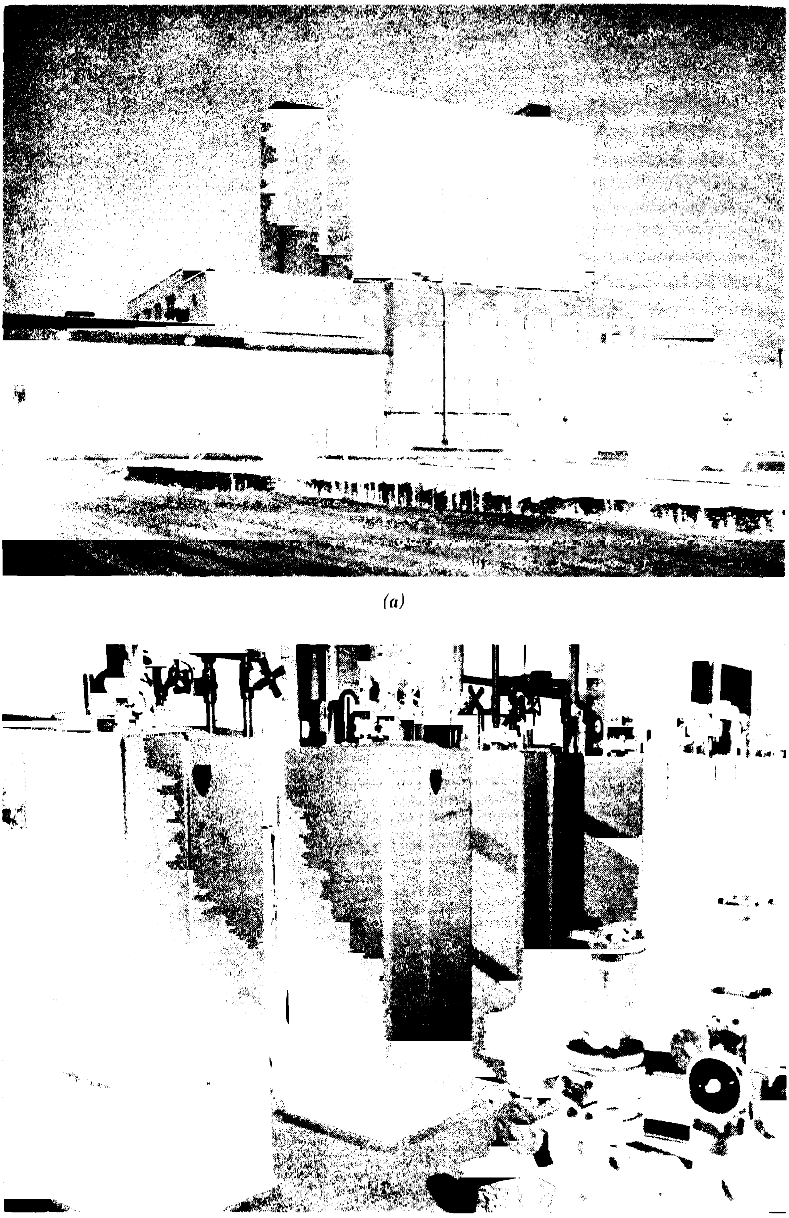
To protect operating personnel and equipment in event of a gas flow during shutdown, air relief discharging to atmosphere is provided. In addition, a vacuum breaker, also connected to an atmospheric vent, is provided to allow air to enter the system whenever the vacuum exceeds a preset amount. Therefore, should an excessive vacuum be created due to the loss of chlorine supply or the absorption of the gas in the system during shutdown, the vacuum breaker will prevent the possibility of water being drawn into the apparatus. These vents, constituting important safety devices, should be kept dry and clear and should be inspected regularly to ensure proper functioning at all times.

Auxiliary equipment which enables automatic control of chlorine dosage has been considerably refined in recent years. Accessories are available which will automatically vary the feed proportional to the flow and quality of the liquid chlorinated or will effect intermittent chlorine dosage where desired.

Where chlorination processes must be continuous, it usually is considered that standby chlorinators should be available. At plants normally requiring a single chlorinator, it is considered good practice to provide one additional chlorinator of equal capacity for use in an emergency. At plants normally requiring two or more chlorinators, a duplicate of the largest unit should be provided, i.e., at least one more chlorinator than the number required for normal maximum demand.

Of equal importance to the provision of standby equipment is the regular, frequent inspection and servicing of all chlorinators, including standby units. Spare parts as indicated by experience and recommended by the equipment manufacturer should be available; this is especially important where standby equipment is not provided at the site.

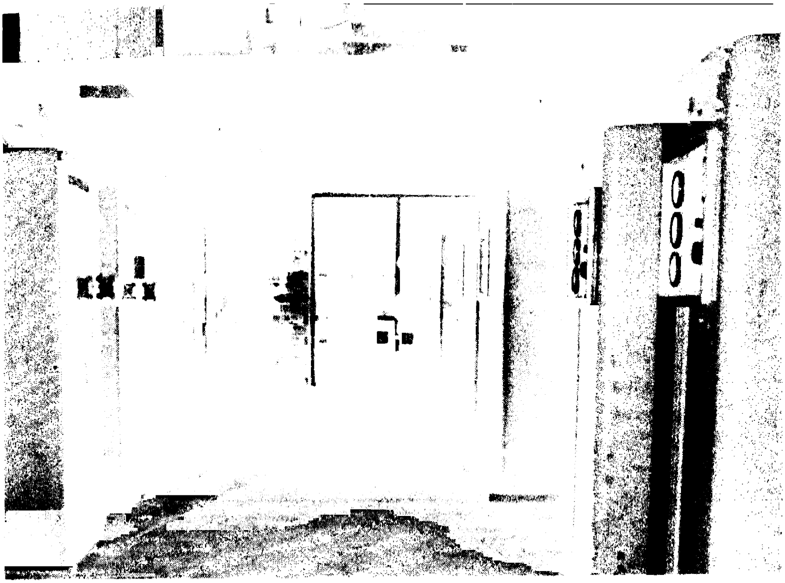
Chlorine Dioxide. Chlorine dioxide, ClO_2, is primarily used in im-



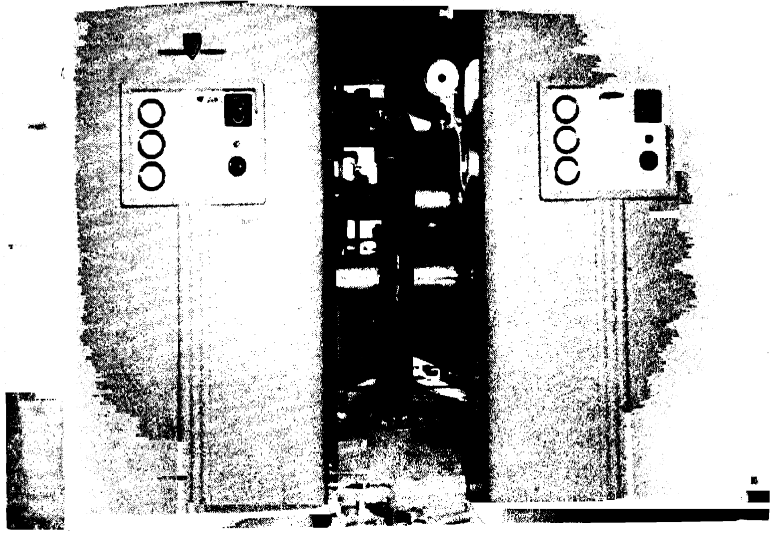
(a)

(b)

Fig. 6 Segments of chlorination system, Torresdale plant, Philadelphia. *(a)* Tank car on track; *(b)* double bank of chlorinators; *(c)* line of evaporators; *(d)* close-up of chlorinators.



(c)



(d)

proving tastes and odors. It is considered by some to be more effective than chlorine in disinfecting water supplies. It is prepared by treating a solution of sodium chlorite, $NaClO_2$, with chlorine in a glass ceramic-packed mixing column. Since chlorine dioxide decomposes very quickly in water, the mixing column is usually located just ahead of the point of application.

Sodium Chlorite. Sodium chlorite, $NaClO_2$, is a dry flaked salt, which, because of its powerful oxidizing nature, is shipped in steel drums bearing an ICC "yellow" label classification. It is stable when sealed or in solution, but is very combustible in the presence of organic material. For this reason the solution should not be allowed to dry out on floors, but should be hosed down with minimum splashing.

Technical sodium chlorite is an orange-colored flaked salt with a density of approximately 56 lb per cubic foot. It is a very powerful oxidizing agent.

Sodium chlorite in contact with acid will react with rapid evolution of chlorine dioxide gas. When heated above 347 °F, sodium chlorite will decompose rapidly, liberating oxygen with the evolution of sufficient heat to make the decomposition self-sustaining. If this decomposition is confined, as in closed containers, the effect is explosive. Therefore, it should be protected at all times from exposure to heat.

Sodium chlorite dissolves easily in water at ordinary temperatures to form an orange-brown solution. This solution is chemically stable under ordinary conditions of temperature and pressure.

As received in loose flake form in metal containers, sodium chlorite will stand considerable rough handling. No danger is involved in the act of scooping or weighing out the material. No health hazard is involved in handling sodium chlorite, other than its being poisonous if taken internally.

Sodium chlorite should be stored only in an enclosed space specially prepared for the purpose and removed from the storage room only as needed for immediate use. Empty containers should be returned to the storage room immediately after each use unless they are shipping containers, in which case they should be thoroughly flushed with water (to the sewer) as soon as they are empty and immediately disposed of at some point well away from any building. Shipping containers should never be used for any other purpose after they are empty.

Rubber gloves and protective clothing should be worn when handling sodium chlorite. If any of the material should come in contact with clothing or other combustible material, such clothing or combustible material should immediately be soaked in water to remove all trace of the sodium chlorite, or it should be taken outside and burned without delay.

Chlorinated Lime. Chlorinated lime, $CaCl(ClO) \cdot 4H_2O$, while primarily used as a disinfectant, is sometimes used in treating water supplies, particularly swimming pools. It is a white powder prepared by chlorinating slaked lime. It decomposes in water, releasing the chlorine for disinfecting action. It contains 39 per cent available chlorine. It should be shipped in corrosion-resistant material and applied as a powder directly to the water to be treated.

Hypochlorites

For this discussion, hypochlorites can be classified as either *dry* or *liquid* in accordance with commercial availability. Calcium hypochlorite is the predominant dry bleach in use in North America and the European continent; it has been widely used for potable and swimming-pool water treatment since its introduction in the late 1920s; lithium hypochlorite recently has been introduced, particularly in the swimming-pool market, as a competitive product. Sodium hypochlorite, of which there are several grades and proprietary forms, is the only liquid hypochlorite disinfectant of note in current use.

Calcium Hypochlorite. Present-day commercial high-test calcium hypochlorite products, introduced in 1928, contain at least 70 per cent available chlorine and have from less than 3 per cent to about 5 per cent lime (which reduces the amount of sludge formed in an aqueous solution). All commercial calcium hypochlorites also contain, among minor amounts of other impurities, some calcium carbonate and other insolubles. In hard water an additional amount of calcium carbonate is formed. Thus, there is some sediment that might be removed from solution, but this is considerably less than the amount formed if bleaching powder is dissolved to obtain a solution of equivalent available chlorine content.

An off-white granular (free-flowing or compressed tablet) material, calcium hypochlorite is, although a highly active oxidizer, relatively stable throughout production, packaging, distribution, and storage. Under normal storage conditions, commercial preparations *lose* about 3 to 5 per cent of their available chlorine content in a year. Contact with water or the atmosphere induces a pronounced increase in the decomposition rate; additionally, it greatly increases the reaction rate with organic materials. Decomposition is exothermic and proceeds rapidly if any part of the material is heated at 350°F, yielding oxygen and chlorine as well as powdery dust which has an irritating action; heat also is evolved which further supports and increases the decomposition rate. The granular form is essentially nonhydroscopic and resists moist caking tendencies when properly stored. Though it is a stable, nonflammable material which cannot be ignited, contact with heat, acids, or combustible, organic, or oxidizable materials may cause fire.

Calcium hypochlorite is readily soluble in water, varying from about 21.5 g per 100 ml at 0° C to 23.4 g per 100 ml at 40° C. Tablet forms dissolve more slowly than the granular materials and provide a fairly steady source of available chlorine over an 18- to 24-hr period.

Granular forms usually are shipped in 35- or 100-lb drums or cartons containing 3¾-lb resealable cans or cases containing nine 5-lb resealable cans. Tablet forms are shipped in 35- and 100-lb drums and in cases containing twelve 3¾- or 4-lb resealable plastic containers.

Because of its strong oxidizing powers and reactivity with organic materials, calcium hypochlorite should preferably be segregated or stored in a location separate from other chemicals or material with which it can react. To minimize loss in available chlorine content attendant upon elevated temperature, cool storage areas should be provided. Containers should be kept dry and should be of a size consistent with use requirements. Stored containers should be so arranged that they can be easily moved from the storage area in event of leaks, and should be located in a darkened area unless the containers themselves shield out excessive light.

Lithium Hypochlorite. Free-flowing granular, dust-free lithium hypochlorite, introduced on the market in the early 1960s and containing about 35 per cent available chlorine, has one advantage over granular calcium hypochlorite forms in that water solutions can be readily formed and are clear when prepared, thus minimizing problems associated with decantation, sludge deposition, etc. Though of comparable stability, cost of the material currently exceeds that of calcium hypochlorite. Its principal market targets are home and commercial laundries and swimming pools. Because of the toxicity of lithium compounds in general, it is not considered safe for use in potable water supplies.

Sodium Hypochlorite. Commercial sodium hypochlorite or liquid bleach, manufactured by hundreds of companies in the United States, some large and many very small, usually contains 12 to 15 per cent available chlorine at the time of manufacture and is available only in liquid form. Its use is generally limited to smaller potable water treatment installations and to swimming-pool water disinfection. It is marketed in carboys and rubber-lined drums of up to 50-gal volume and in trucks. Household products, containing from 3 to 5¼ per cent available chlorine, are packaged in brown or amber-colored glass or polyethylene bottles.

Regardless of how they are produced, all NaOCl solutions are unstable to some degree and deteriorate more rapidly than calcium hypochlorite. The effect can be minimized by care in manufacturing processes and by controlling the alkalinity of the solution: greatest stability is attained with a pH close to 11.0 and with the absence of heavy metal cations. Storage temperatures should not exceed about 85 °F; above that level, the rate of decomposition rapidly increases (possibly of the magnitude of doubling with each 10 °F increase). Storage in a cool, darkened area very greatly limits deterioration rate, but most large manufacturers recommend a maximum shelf life of 60 to 90 days.

All hypochlorite solutions are corrosive to some degree and affect the skin, eyes, and other body tissues that they contact. Accordingly, rubber gloves, aprons, goggles, and similar suitable protective apparel should be provided for preparing and handling hypochlorite solutions. Areas of skin contact should be promptly flushed with copious quantities of water. Every precaution should be observed to protect containers against physical damage, to prevent container breakage, and to minimize accidental splashing.

The Feeding of Hypochlorites. Hypochlorites are usually quite soluble in water, but in solution are quite corrosive. They are usually applied in small installations where the solutions are made up in stoneware crocks. The solution is then fed to the point of application through a chemical proportioning pump which is made of corrosion-resistant materials. The solution is usually transmitted through rubber hoses or small plastic pipes. There are on the market some hypochlorite feeders that are designed to operate by water pressure. These are not as dependable as the electrically operated proportioning pumps. Because of the hazards of large chlorine installations some utilities that have used chlorine as a slime-control agent in the condensers of their power plants have now resorted to the use of hypochlorites for this purpose. However, they are obtaining the hypochlorites direct from the manufacturer in solution form and feeding it through noncorrosive lines after metering with a chemical proportioning pump.

Ozone. Ozone, O_3, is a faintly blue gas of pungent odor. It is a form of oxygen with 3 atoms to the molecule. It is unstable, breaking down readily to normal oxygen and nascent oxygen. The latter is a powerful oxidizing agent. It also has germicidal action. It is usually produced by passing high-voltage electricity through dry atmospheric air between stationary electrodes. A small percentage of the oxygen in the air is converted into ozone in treatment. It is usually injected into the water in a highly baffled mixing chamber. The ozone residual is determined by the use of the ortho-tolidine test (0.1 ppm ozone = 0.15 ppm Cl_2).

Lime. Some water plants use either quicklime, CaO, or hydrated lime, $Ca(OH)_2$, for sterilizing purposes. Care should be used in interpreting the results. The properties of these materials will be described fully under "Softening," later in this chapter.

Silver. Silver, Ag_2, has been used in the sterilization of water on rare occasions. A form of activated silver known as Katadyn sand filter has been on the market since 1929. Another method of introducing the metal into the water is by the passage of an electric current through the metal into the water. This process has been used principally in swimming pools.[1]

Dechlorinating Agents

Activated Carbon. Activated carbon is a form of charcoal that has been treated so as to make it highly absorbent of various materials. It is available in two forms, powdered and granulated. It has a fairly high affinity for absorbing chlorine. Powdered carbon is seldom used for dechlorination, but high dosages have a dechlorinating effect. Many plants use granulated carbon in pressure filters to dechlorinate water that has required heavy chlorination. In the presence of moisture it can produce excessive corrosion of iron and steel. Rubber-lined pipes or copper or plastic lines are used for transmitting the carbon suspensions. Pressure filters for granular carbon should be lined with a suitable protective coating. Further details on the properties of activated carbon will be found in the section on tastes and odors.

Aluminum Ammonium Sulfate. The properties of ammonium alum, $AlNH_4(SO_4)_2 \cdot 12H_2O$, were described in the section on coagulants. As a dechlorinating agent it would convert the chlorine to chloramines.

Ion-exchange Resins. The synthetic resins are sometimes used as dechlorinating agents, but usually on a very small scale. The resin for this purpose must be very carefully selected, as only certain types have a marked degree of efficiency. The suppliers of these materials are usually well acquainted with which type of resin would be the most effective in absorbing chlorine in water.

Sodium Bisulfite. The principal constituent is sodium pyrosulfite, $NaHSO_3$, or sodium metabisulfite, $Na_2S_2O_5$. These white, crystalline powders are readily soluble in water and may be applied to the water with conventional dry-feed equipment.

Sodium Sulfite. Sodium sulfite, Na_2SO_3, is similar in appearance and use to the above.

Sulfur Dioxide. Sulfur dioxide is produced in North America either by the combustion of sulfur in special burners, by burning pyrites, or as a by-product of smelting operations. The gas so produced is purified by passing it into water, which dissolves it and certain impurities. This liquor is then heated to vaporize the gas which is subsequently dried and compressed into liquid form.

Various physical and chemical properties of sulfur dioxide, a chemical compound, are summarized in Table 17-1. In the gaseous state, sulfur dioxide is colorless and is about 2.26 times as heavy as air. The liquid, also colorless, is about 1.44 times as heavy as water. Unconfined liquid sulfur dioxide rapidly vaporizes to gas.

Sulfur dioxide is slightly soluble in water (about 20 times the solubility of chlorine), up to about 20 per cent by weight at 32 °F, dissolving to form a weak solution of sulfurous acid. Because its vapor pressure increases with rising temperature, its solubility decreases with increasing temperatures; at 80 °F, it is soluble to less than 10 per cent.

Dry sulfur dioxide, liquid or gas, is not corrosive to steel and other common metals; however, in the presence of sufficient amounts of moisture it is corrosive to most common metals. Among materials that have proved suitable are aluminum, brass, various bronzes, copper, and certain alloys such as Chlorimet, Durco D-10, Hastelloy C, Haveg, stainless steels, etc. For handling aqueous solutions, Haveg, lead, type 316 stainless steel, No. 20 stainless steel, and Teflon are recommended; zinc and galvanized materials are not suitable.

Sulfur dioxide is neither flammable nor explosive in either the gaseous or liquid state. In fact, it is an effective fire-extinguishing material, but other properties preclude its use for this purpose. Because it neither burns nor supports combustion there is no danger of fire or explosion due to igniting gas or liquid.

Sulfur dioxide may be fed by several types of equipment used for other compressed gases. This includes rotameters, orifices equipped with manometers, and the vacuum-type chlorinators. In many temporary installations it is allowed simply to bleed from the cylinder through a hose to the point of application at a rate that is set with the cylinder valve. The cylinder may be placed on a platform scale so that the loss of weight may be measured. This also aids in setting the rate of feed.

Sulfur dioxide is an extremely irritating gas which, like chlorine, readily elicits respiratory reflexes by exposed persons. The gas may cause varying degrees of irritation of the mucous membranes of the eyes, nose, throat, and lungs due to sulfurous acid formation in the presence of moisture. Concentrations of 3 to 5 ppm can be readily detected by most persons; in higher concentrations the severely irritating effect of the gas makes it unlikely that any person will remain in a sulfur dioxide–contaminated atmosphere unless he is unconscious or trapped. Contact with the liquid results in a freezing action on the skin; when unconfined in a container, it rapidly vaporizes to gas producing the aforementioned effects.

The ACGIH has established the 8-hr, time-weighted (threshold limit) concentration at 5 ppm or approximately 13 mg per cubic meter. Concentrations exceeding 50 to 100 ppm for 30 to 60 min are dangerous, and concentrations of 500 ppm are acutely irritating to the upper respiratory system and cause a sense of suffocation even with the first breath (see Table 17-2). There is no evidence that exposure to allowable concentrations produces a cumulative effect.

HYDROGEN-ION (pH) ADJUSTMENT

Calcium Carbonate. (See "Coagulant Aids.")

Carbon Dioxide. (See "Softening.")

Hydrochloric Acid. Hydrochloric acid, HCl, is a clear-colored or slightly yellow fuming, pungent liquid. It is also poisonous and may contain iron or arsenic. If it is to be used in a potable water supply, care should be taken to obtain the purified form (U.S.P.). It can be shipped in glass bottles, carboys, rubber-lined steel drums, rubber-lined tank cars, or trucks. It contains approximately 35 per cent available hydrogen chloride. To reduce the fuming characteristic it should be diluted (*by adding the acid to water*) to approximately 20 per cent HCl. After dilution it may be fed in any reasonably accurate corrosion-resistant liquid-chemical feeding device. It is not often used in the treating of potable water supplies because this use increases the chloride content of the water. The hazards are those of any strong acid which causes burns. Contact with the skin should be avoided, and protective equipment for the eyes, face, and hands should be worn when handling this material.

Lime (quicklime and hydrated lime). (See "Softening.")

Sodium Carbonate. $Na_2CO_3 \cdot H_2O$—soda ash. (See "Softening.")

Sodium Hydroxide. Caustic soda, NaOH, is available in the liquid form in two concentrations, 50% NaOH and 73% NaOH. It is also available as solid caustic soda containing 100% NaOH. The 50% caustic soda begins to crystallize at approximately 54 °F and the 73% concentration at about 145 °F. These materials are usually shipped in insulated tank cars and quite often arrive at the receiving point still in liquid form. However, such tank cars are usually provided with coils for steam heating. Care should be taken when unloading the caustic soda to follow the manufacturer's manual for such procedure in every detail. In climates where storage temperatures are below the solidification point for the grade of caustic soda received, the material should be diluted on unloading to a concentration that will not solidify. Consulting the manufacturer's manual will show the proper procedure for doing this. If the solid form of caustic soda is received, it is usually dissolved immediately on receipt. A caustic soda solution may be fed by conventional liquid-chemical feeding equipment. The handling of caustic soda in all forms involves a number of extreme hazards. In the dilution process, considerable heat is generated, so the rate of dilution and the methods of cooling should be carefully controlled so that there is no boiling or splattering of the liquid. Caustic soda will cause severe burns to the skin and eyes, so complete protective equipment is necessary. This includes head covering, respirator with goggles, cotton clothing (caustic soda will dissolve wool), button collar, rubber apron, sleeves over rubber gloves, and trousers over rubber work shoes.

Sulfuric Acid. Sulfuric acid, H_2SO_4, is a strongly corrosive, dense, oily liquid, colored clear or dark brown, depending on purity. It should be of the U.S.P. grade, free of heavy metals. It is available in a number of grades, containing from 60 to 94% H_2SO_4. In the 93% grade it is noncorrosive to steel drums, tank cars, or tanks. Once diluted, it is highly corrosive and should be contained in rubber-, glass-, or plastic-lined equipment to the point of application. It causes severe burns and will decompose clothing and shoes. Complete protective equipment is necessary in handling sulfuric acid. It may be fed with any corrosion-resistant (rubber-covered) liquid-chemical feeding device.

FLUORIDATION AND FLUORIDE ADJUSTMENT

Fluoridation[2]

Ammonium Silico-Fluoride. Ammonium silico-fluoride, $(NH_4)_2SiF_6$, is produced by neutralizing hydrofluosilicic acid with either aqua or anhydrous ammonia. It is sold as a white, odorless, free-flowing crystalline material. One hundred per cent will pass a 20-mesh screen, and 90 per cent will be retained on a 100-mesh screen. Its solubility is high, comparing favorably with sodium fluoride. It is available in 100- and 400-lb drums. It can be fed through conventional dry-feed equipment, but dust-collecting equipment must be provided. This solution can be transmitted through standard chemical solution lines.

Fluospar. Fluospar, CaF_2, is the principal source of the commercial fluoride compounds available at the present time. Pure fluospar is a lustrous glasslike material, almost always translucent or transparent, and may be colorless or range in color from blue to red. Fluospar may be used as a direct source of fluorine for the fluoridation of water supplies. It may be dissolved by using alum solution.[3] This is considered the most economical chemical of the various fluoride compounds. It is available in three general grades of purity. The best grade for fluoridating purposes should contain at least 85% CaF_2 and less than 5% silica. It may be shipped in bags, drums, or in bulk in hopper cars or trucks. The hazards are those of a chemical dust, with some danger of etching glass if moisture is present.

Hydrofluoric Acid. Hydrofluoric acid, HF, is a clear, pungent, fuming, mobile, corrosive liquid. It is poisonous, dangerous, and produces terrible sores when allowed to touch the skin. Its only use in fluoridating water supplies was at Madison, Wisconsin, where it has since been discontinued. It is produced by the acidification of fluospar.

Hydrofluosilicic Acid. Hydrofluosilicic acid, H_2SiF_6, is a 20 to 30% water solution of H_2SiF_6. It is a colorless, transparent, fuming, corrosive liquid, having a pungent odor and irritating action to the skin. When vaporized, the acid decomposes to hydrofluoric acid and silicon tetrafluoride. The liquid acid has a tendency to break down in this manner at the packing glands of piston pumps. The silicon tetrafluoride has a further tendency to break down, depositing colloidal silica, SiO_2. This material tends to abrade even the hardest metal pistons. Therefore, oil diaphragm pumps are necessary for handling it. This acid is manufactured from gases that are produced when phosphate rock is acidified in the manufacture of phosphoric acid. The gas, silicon tetrafluoride, SiF_4, is very corrosive and will destroy vegetation. The manufacturers of the phosphoric acid (principally the fertilizing industry) are not allowed to discharge this material into the atmosphere. Therefore, the process gases are run through scrubbing towers, and the silicon tetrafluoride is absorbed into water. This produces a weak solution of hydrofluosilicic acid. This weak acid is concentrated to solutions varying in strength from 23 to 30% H_2SiF_6. The commercial product may have a straw or slightly reddish color, due to dissolved iron. In the amounts used in water fluoridation, this presents no problem. The acid is quite corrosive, and rubber-lined or plastic equipment should be used for shipping, unloading, storing, and feeding. The acid is only slightly volatile. It is a vapor that can cause irritation of the respiratory system. Equipment or glass exposed to the fumes tends to become corroded or etched. Adequate ventilation should always be provided. Complete protective equipment should be provided for handling it. Rubber gloves, goggles or face shields, rubber apron, rubber boots, lime slurry barrels, epsom salt solution, and safety showers are all necessary.

Since this material is a by-product of the fertilizer industry, it is becoming available at increasingly lower prices. In a completely enclosed, corrosion-resistant system, it is much more foolproof against accidents in handling than the other fluoride compounds.

Sodium Fluoride. NaF is produced by neutralizing hydrofluoric acid with either sodium carbonate or sodium hydroxide. It is available as crystals or white powder. It is highly soluble in water, which increases its use in the fluoridation of water supplies. It is comparatively expensive. It is relatively noncorrosive, although in the presence of moisture it tends to give off a smell of hydrogen fluoride fumes. It is available in bags or in bulk and may be fed in conventional dry-feed equipment, which must be provided with dust-collecting equipment. The hazards are those of any chemical dust, except that this material is extremely poisonous and glass exposed to its dust will be etched.

Sodium Silico-Fluoride. Sodium silico-fluoride, Na_2SiF_6, is a white, free-flowing, odorless crystalline powder. It is produced by neutralizing hydrofluosilicic acid with soda ash, Na_2CO_3, or sodium hydroxide, NaOH, and evaporating the resultant solution. Its use permits many small fertilizing manufacturers to recover their hydrofluosilicic acid without expensive concentration equipment. It is by far the most extensively used compound in the fluoridation of water supplies because of its availability and cheapness. Its disadvantages lie in its very low solubility, 60 gal of water being required to dissolve 1 lb of sodium silico-fluoride. It may be shipped in paper bags, paper-lined barrels, or wooden-fiber drums. It can now also be shipped in bulk, in hopper railroad cars, or in trucks. If the paper bags or paper-lined barrels are stored for any length of time, the paper tends to char. Certain grades of the material are more suitable for measuring in a chemical dry feeder, which must be equipped with a dust-collecting system (see AWWA Standard B702-71). With a dry feeder it is measured into a solution box, and the solution is then transmitted through corrosion-resistant lines to the point of application. The hazards are those of any chemical dust, plus the corrosive effect of a small amount of HF on hydrolysis.

Fluoride Adjustment Agents

Activated Alumina. Al_2O_3 is a highly porous and granular form of aluminum oxide, having a preferential adsorptive capacity for moisture from gases, vapors, and some liquids. It is also used as a carrier to remove fluorides from drinking water. It is in use for this purpose at Bartlett, Texas, and at the Army water plant at Camp Irwin near Barstow, California. When the aluminum becomes saturated with fluorides, it must be regenerated. This is accomplished by first backwashing with water in order to remove the accumulated solids. The fluorides are removed by backwashing with a weak caustic solution. The residual caustic is then neutralized with a weak acid which is followed by water rinses. Activated alumina is available in granules ranging in size from a powder to lumps of approximately 1½ in. The 8- to 14- and the ¼- to ⅛-in. mesh sizes are most generally used. Activated alumina may be shipped or stored in any type of container, such as burlap, paper bags, drums, or in bulk. In the fluoride-removal process, the water is percolated through beds of alumina. These can be pressure filters piped for backwashing and regeneration.

Fluo-Carb. This is a trade name. It is a granular bone-charcoal product for the removal by adsorption of excess fluoride ions. It is a dry material of 30 to 50 mesh size and may be regenerated by caustic soda and sodium bisulfate.

Fluorex. This is another trade name. This is a tricalcium phosphate which is also for the purpose of removal of excess fluoride.

Magnesium oxide. MgO is usually added in the form of a lime that is high in magnesium content. Both the fluorides and the precipitated magnesium hydroxide are removed by settling and then discarded.

Sodium Bisulfate. Sodium bisulfate, $NaHSO_2 \cdot H_2O$, is limited primarily to removing fluorides in certain mineral compositions that have no known application in the water-treatment field.

TASTES AND ODORS

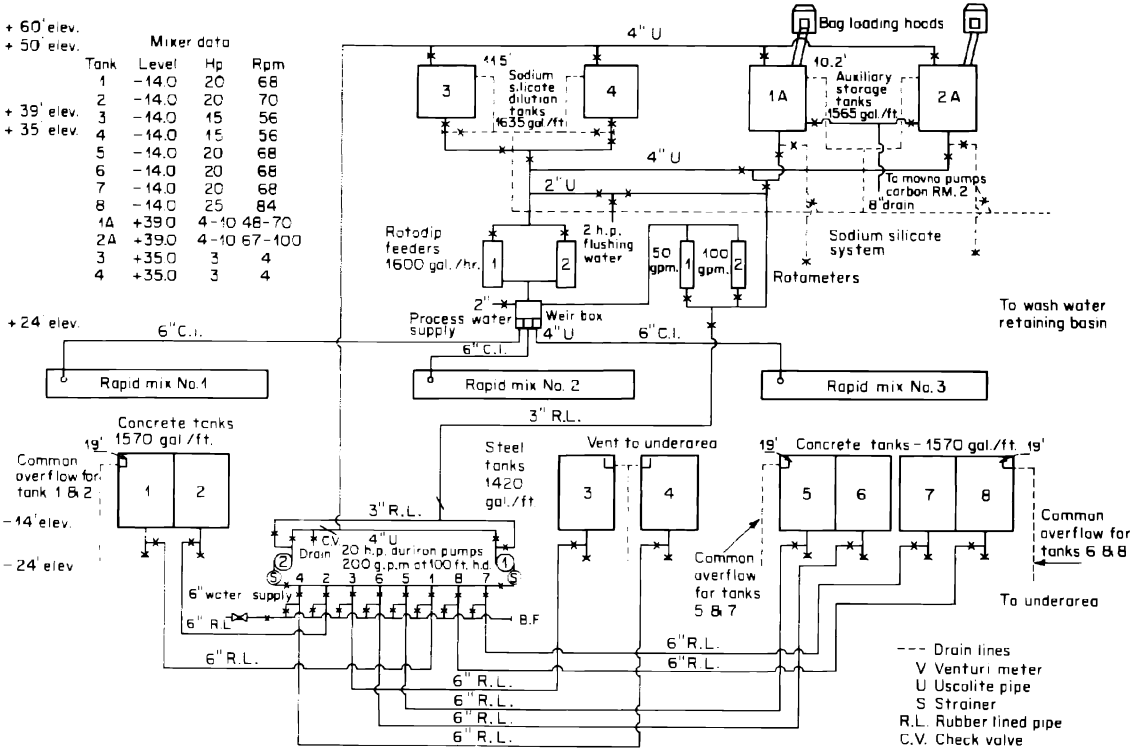
Activated Carbon (Powdered and Granular)

Activated carbon is a form of charcoal that is activated by a carefully controlled combustion process to obtain carbon possessing the properties necessary to adsorb taste- and odor-causing substances from water. The activation process develops a carbon structure with a large surface area. Normal water-grade carbon has a specific surface area ranging from 500 to 600 sq m per gram. The active carbon particles appear to be solids, but are actually honeycombed with an infinite number of minute tunnels or pores which are on the order of molecular size, and their dimensions are expressed in angstrom units (Å). The materials responsible for tastes and odors in water which might be the products of industrial waste, sewage, and plant and animal organisms are thought to be adsorbed in pores not greater than 20 Å in diameter. In the highly activated carbons about 75 per cent of the surface area consists of pores of less than 20 Å in diameter.

Activated carbon is prepared from wood charcoal, paper char, petroleum coke, lignite, peach pits, coconut husks, and other carbonaceous materials. The carbons used in the water industry are prepared principally from paper char, hardwood charcoal, or lignite. The activated carbon is available in two forms, powdered or granular. The powdered material is a very finely ground material where over 90 per cent passes a 300-mesh screen (see AWWA Standard B-600-66). Granular activated carbon is ground and screened to any desired size. In the size used in water-treatment plants, 100 per cent will pass an 8-mesh screen, and at least 90 per cent will be retained on a 12-mesh screen. The active carbon is available in paper bags or in bulk (drums or steel containers) or in covered hopper railroad cars. A recent development is a delivery of powdered carbon in airslide hopper cars or trucks. In these units the carbon is first fluidized by subjecting the unit to a low air pressure (2 to 5 psi), and then the fluid carbon is allowed to flow at the desired rate into the receiving tank. This method is now being used only at plants equipped with a slurry system. The carbon receiving tanks are usually square concrete structures equipped with propeller or turbine mixers and are of sufficient size to hold the dry contents of a hopper car or truck as a slurry. Sufficient water is placed in the tank to fill it close to half full (at least 18 in. above the top mixer paddle), and one-half of the car is unloaded into the tank with the mixer in operation. More water is then added, and the car shifted so that the second half may be unloaded. After the unloading is completed, water is usually added to bring the resultant slurry up to the desired concentration of 1 lb per gallon. The slurry may then be transferred to feeding tanks or slurry storage by rubber-lined or silicon-iron centrifugal pumps. The piping for conveying the slurry should be either rubber- or plastic-lined steel or PVC pipe. The carbon slurry may be fed to the water by volumetric metering devices or by valveless proportioning pumps. All mechanisms handling carbon suspensions or slurries should be either rubber-covered, plastic-lined, stainless steel, or of silicon-iron composition.

The dry powdered carbon may be fed in the conventional chemical dry feeder. Since the angle of repose for dry carbon is approximately 40°, it is suggested that hoppers for feed machines and storage be built with walls at a 60° angle to the horizontal to ensure free gravity flow. All mechanisms for handling the dry material should be tightly sealed to confine the dust. Dust-collector equipment should be used whenever deemed necessary. Normally, the dry carbon is measured at a set rate into a mixing tank, where it is converted into a thin suspension in water. It is then transmitted by piping to the point of application. The mixing or solution box beneath the feeding mechanism should be capable of wetting down and carrying away the carbon under maximum feeding conditions. Vortex bowls have been found satisfactory. Water jets or sprays are always a worthwhile adjunct. A water ejector should always be used to carry the wetted carbon away from the machine. If possible, the carbon-feeding machines should be isolated from other parts of the plant.

Most water plants using reasonably large quantities of activated carbon now convert it to the slurry form when received. It is even quite feasible to dump the bag carbon into a tank equipped with a turbine mixer from which point it can be fed through the usual slurry feeding devices. The feed line carrying the carbon suspension from the feeding machine should be of ample size to handle the volume of water required for dilution. If possible, the line should be installed with a continuous downgrade to the point of application. Provision should be made for cleaning out any carbon which may settle in the line and cause clogging. Whenever the feeding is stopped for any reason, the line should be flushed with clear water. In many smaller plants a rubber hose has been used for the entire feed line, so that stoppages may be easily eliminated by manipulation. Numerous tests have demonstrated that there is no loss of adsorptive activity when carbon is held in water as a slurry over long periods of time (up to 1 year). Mixing equipment used to wet and slurrry activated carbon is under evaluation at several cities. It appears that the slower type of mixing is giving way to rapid mixing, with the agitator operating at 60 to 70 rpm. Agitators normally consist of two sets of stainless steel paddles, one set near the bottom of the tank and one set placed approximately 10 ft from the bottom. With such an arrangement, the activated carbon can be slurried almost as rapidly as it is discharged from the hopper car. With the proper equipment, tests have shown that an airslide car containing 21 tons of carbon can be unloaded in less than 1 hr. Water plants purchasing less-than-carload quantities of powdered activated carbon may also find the slurry system very desirable. When a bag shipment is received, for instance, the bags can be emptied directly into a slurry tank, thus reducing much of the handling associated with bag storage. The tank size required to slurry less-than-car-



Mixer data

Tank	Level	Hp	Rpm
1	−14.0	20	68
2	−14.0	20	70
3	−14.0	15	56
4	−14.0	15	56
5	−14.0	20	68
6	−14.0	20	68
7	−14.0	20	68
8	−14.0	25	84
1A	+39.0	4–10	48–70
2A	+39.0	4–10	67–100
3	+35.0	3	4
4	+35.0	3	4

Fig. 7 Schematic drawing of a carbon slurry system. South water filtration plant.

load or -truckload shipments can easily be determined—that is, a 1,000-lb carbon shipment would require a tank having a usable capacity of 1,200 gal when a slurry concentration of 1 lb per gallon is used. Figure 7 shows a carbon slurry system using rapid mix.

Potassium Permanganate ($KMnO_4$). This material is in the form of black or purple crystals having a blue metallic sheen, a sweetish, astringent taste, and no odor. It is highly soluble in water, which makes for easy application. However, in large quantities it presents a fire hazard. Explosions are liable to occur when it is brought into contact with organic or readily oxidizable materials, either in solution or in the dry state. It is usually made up in dilute solution (1–4%) as needed for application. It may be fed with the usual chemical metering pump. It is available in drums of 110 or 600 lb, or in bulk in railroad hopper cars or hopper trucks. It can be stored in the usual chemical storage bins and fed with the conventional dry-feed equipment. However, the solution feed as described in the paragraph above gives more accurate control of the permanganate feed. Users of this material for taste and odor control should consult the supplier as to methods and techniques.

Where taste and odor problems or levels are high and variable, powdered carbon treatment is considered more efficient. Reports from the National Board of Fire Underwriters state that the activated carbons normally used in water treatment have no dust explosion hazard and are not subject to spontaneous combustion when confined in bags, drums, or storage bins. However, the carbons are combustible and can be burned or will ignite when a sufficiently high temperature is applied. The ignition point of the activated carbons will vary from 600 to 800 °F. After ignition, activated carbon will not burn with a flame, but will glow or smolder and continue to do so until all of the carbon material is oxidized. Storage of carbon in paper bags does present a hazard, in that paper will burn more rapidly. Bags of powdered carbon should be stacked in rows with aisles between in such a manner that each bag is accessible for removal in case of fire. In case of an activated carbon fire, the safest procedure, if possible, is to place the smoldering material in a metal container and haul it outside the building. A smoldering carbon fire may also be smothered by means of a very fine spray or mist of water from a hose or by a foam-type chemical extinguisher. Do not attempt to extinguish the carbon by a direct stream of water, as this will cause the light, smoldering particles to fly into the air and spread the fire. An overhead sprinkler system installed in the storage and feeding rooms is a practical precautionary measure. Activated carbon should not be stored where it can come into contact with gasoline, mineral oils, or vegetable oils. This material, when mixed with carbon, will slowly oxidize until the ignition temperature is reached. Never mix or store carbon with such materials as chloride of lime, hypochlorites, sodium chlorite, or potassium permanganate. Such mixtures are known to be spontaneously combustible. Activated carbon is an electrical conductor and should not be allowed to accumulate as dust near or on open electrical circuits. Some activated carbons are subject to deterioration in storage, so that carbon storage areas should be relatively free of such air contaminations as sulfur dioxide, chlorine, hydrogen sulfide, organic vapors, etc. Normal safety practices have shown that protective clothing, respirators, neck cloths, gloves, and goggles should be provided for workers handling powdered activated carbon.

Granular carbon is usually placed in pressure filters through which the entire flow of water passes, so that any objectionable tastes and odors may be removed. This method of treatment is usually applied after filtering, so that the granular carbon bed will not become clogged or coated with colloidal material from the unfiltered water. Since the time of contact with this type of treatment is usually short, the general effect of the use of granular carbon filters in taste and odor removal is that of a polishing action. Where the taste and odor problems are fairly constant and at a low level granular carbon filters are quite satisfactory. They have one adverse effect, that of removing the free residual chlorine in the water.

MINERAL OXIDATION (IRON AND MANGANESE)

Chlorine, Chlorine Dioxide, Ozone, Potassium Permanganate. (See "Disinfection" and "Tastes and Odors.")

STABILIZATION AND CORROSION CONTROL

Quicklime, Hydrated Lime, and Sodium Carbonate. (See "Softening.")

Sodium Hexa-Metaphosphate. $Na_{16}P_{14}O_{43}$ is one of several forms of what are known as "glassy" phosphates, available from any number of manufacturers in both the powdered and granular form. It is used in water softening and in boiler water treatment. It is also used as a sequestering agent in municipal water supplies. It is available in 100-lb multiwall paper and net burlap bags. It is infinitely soluble in water. Solutions are usually prepared in a mixing tank to a definite concentration. The resultant solution may be fed by a liquid chemical metering device through either hard rubber, plastic, or stainless steel lines.

Sodium Carbonate. (See "Softening.")

Sodium Tri-Polyphosphate. $Na_5P_3O_{10}$ is available in both the powdered and granular form and may be shipped in 100-lb multiwall paper bags or in fiber drums. This material is primarily used in water softeners. It has a limited solubility in water and insofar as is known is not added to municipal water supplies.

SOFTENING

Carbon Dioxide. CO_2 may be produced by the burning of carbonaceous materials such as wood, coal, coke, fuel oil, or gas. Another kind of carbon dioxide generator is known as the "pressure-type CO_2 generator." In this the ratio of fuel to air is so carefully regulated that complete combustion takes place. The pressure in the combustion chamber forces the gas to the CO_2 diffusers.[4] Better diffusion of the CO_2 is obtained by forcing a water spray against the gas as it is released from the diffuser openings, thus breaking up the bubble and ensuring better control. In a method now being offered to the waterworks industry, gas and air are burned together in subsurface burners, thus producing carbon dioxide at the point of application. Carbon dioxide is a clear, colorless gas that becomes liquefied under pressure and solidified by releasing the pressure. The expansion produces a frost that is compressed into cakes known as "dry ice." Carbon dioxide may be obtained in bulk as a liquid under pressure from certain chemical suppliers. It must then be vaporized and diffused into the water at the point of application. This procedure is quite expensive and most users prefer to obtain their carbon dioxide by "on-the-spot" combustion. Carbon dioxide is a colorless, odorless gas of high specific gravity. When unconfined it tends to seek the lowest level possible. Its chief hazard is the danger of producing suffocation. In water, its solution produces carbonic acid which is highly corrosive to iron and steel. It may be transmitted to the point of application in ordinary pipes, but the diffuser pipe should be of noncorrosive material. Several manufacturers offer what are called "recarbonation" systems for the generation and feeding of carbon dioxide. Some of these are quite adequate (see Fig. 8).

Ion-exchange Resins. The most widely used ion-exchange resins are of the cation-exchange type. This type is available as both a greensand and a synthetic gel. The greensands are available in two forms, one with a hardness removal capacity of 2,800 grains per cubic foot, the second type with a capacity of 5,500 grains per cubic foot. The synthetic gel resins range from a capacity of 7,000 grains per cubic foot for the phenolic type to 30,000 grains per cubic foot for the nonphenolic type. Some of the new polystyrene base exchanges have capacities of 18,000 to 30,000 grains of hardness removal per cubic foot of material. These have a low rate of attrition, so the replenishment cost is lower than with most other base-exchange materials. Softening by cation-exchange techniques may be accomplished in either closed or open containers in which the cation resin bed acts as a filter through which all of the water is percolated. The containers are so arranged that the resin bed may be regenerated with brine solution. Piping must also be arranged so that the filters may be backwashed with water either as a routine measure or as a means of removing residual amounts of brine. Where resin filters of the open or pressure type are used as downflow filters, they tend to collect colloidal matter such as iron, unsettled flocs, or colloidal clay on the resin grains, thus limiting useful life of the resin. Often such filters are preceded by sand filters which remove this colloidal matter from the water before it reaches the resin beds.

The cation-exchange resins are base-exchange resins in which, when being regenerated with sodium chloride, the sodium is exchanged for the calcium or magnesium that has been removed from the water in the softening process. In softening, the reverse reaction takes place, and this gives the softened water a high sodium content.

Quicklime and Hydrated Lime. Quicklime, CaO, is a product resulting from the calcination of limestone or its equivalent, such as dried-water softening sludge of suitable analysis, and consists essentially of calcium oxide in natural association with a lesser amount of magnesium oxide. Hydrated lime, $Ca(OH)_2$, is a very finely divided powder resulting from the hydration of quicklime with enough water to satisfy its chemical affinity. It consists essentially of calcium hydroxide or a mixture of calcium hydroxide and magnesium hydroxide, depending on the type of quicklime used in slaking.

The revised standards for quicklime and hydrated lime (AWWA Standard B202-65) give detailed recommendations on impurities and particle sizes. These standards recommend for quicklime the minimum of 90 per cent available calcium oxide content. Hydrated lime should have a minimum available calcium oxide content of 68.0 per cent or more. Quicklime is available in whatever particle size is required by a given installation and

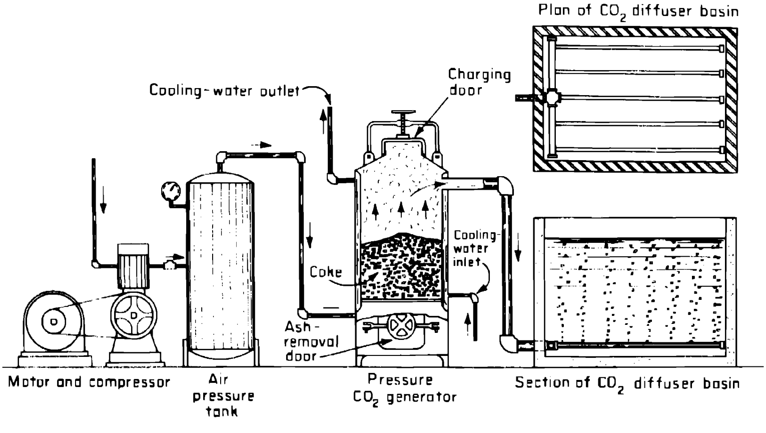


Fig. 8 Recarbonation system. (*National Lime Association booklet, Washington, D.C., April, 1957.*)

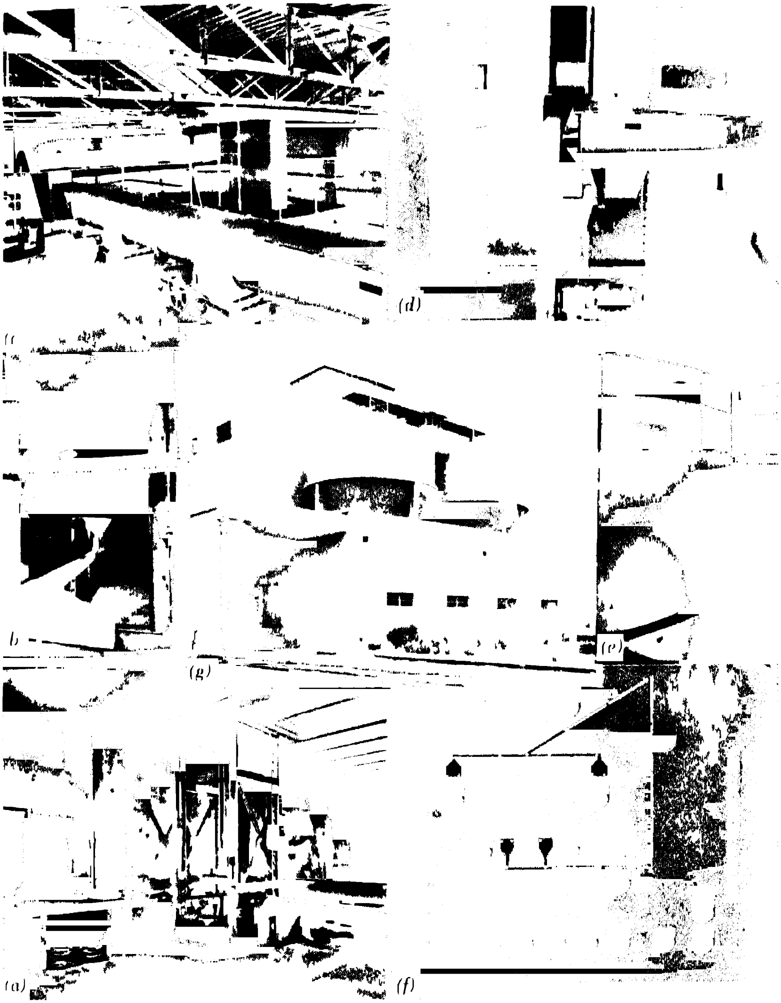


Fig. 9 Lime-handling system, Elm Forks plant, Dallas. *(a)* Bag lift for alternate use, *(b)* conveyor from railroad tracks to bucket elevator, *(c)* arrangement for conveying lime to four silos on fifth floor, *(d)* discharge from railroad screw conveyor to bucket elevator, *(e)* bucket elevator connection to screw conveyors for filling silos, *(f)* electric flow-control panel, *(g)* outside lime storage silos. *(Courtesy of M. L. Horton, Link Belt Co.)*

is usually specified in each particular contract. Hydrated lime is a powder that should be uniform in size.

Methods of Handling Quicklime is available in 50-lb bags and in bulk. Most quicklime is usually shipped in covered railroad hopper cars or, more recently, in bulk-material trucks. The unloading may be accomplished by mechanical devices of two general types: the purely mechanical, consisting of bag lifts, screw conveyors, and bucket elevators (see Fig. 9); and the pneumatic type, in which high-powered air compressors suck the material into a dumping mechanism which drops the material through a series of trap doors into other screw conveyors. These conveyors take the materials to the silos or storage bins. Both types are satisfactory and the choice of system is usually based on cost and the local situation. Lime is not a corrosive material and may be stored in concrete or steel silos or bins. There is a tendency to cake on long standing, so adequate means of breaking up the caking, such as vibrators behind steel plates, should be provided. There is some tendency of the quicklime to air slake, so exposure to outside air should be kept to a minimum. Hydrated lime tends to absorb carbon dioxide from the atmosphere even in the slurry form, and in this case exposure to outside air should be carefully controlled. Hydrated lime may be stored in paper bags for a considerable time without excessive absorption of carbon dioxide or moisture. Hydrated lime is now available in bulk. It is delivered in and unloaded from "blower" trucks (see Fig. 10). In unloading, the hydrated lime powder is fluidized by an air compressor up to 10 lb psi. In the preparation of lime slurry, the fluidized stream is discharged into a receiving line containing water jets. The wet-down lime is carried down into a tank containing water and equipped with a turbine mixer. The resulting slurry may be built up to as much as 42 per cent hydrated lime which still can be fed by a valveless proportioning pump.

Quicklime is normally made into a thin suspension called "milk of lime,"

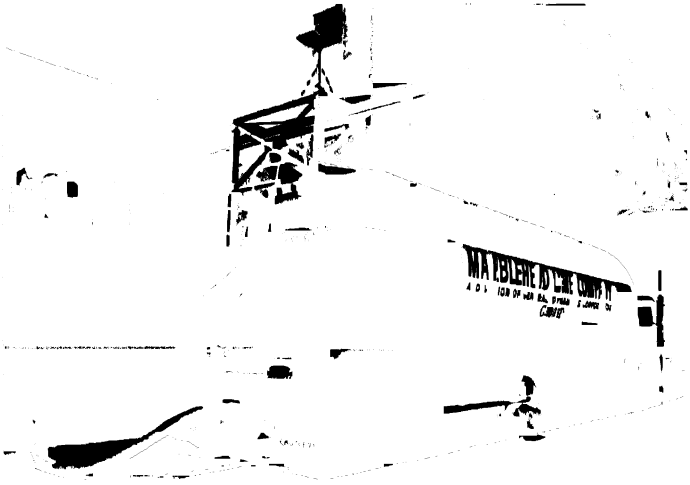


Fig. 10 Blower truck for hydrated lime, South District filtration plant.

containing approximately 5 per cent calcium hydroxide, $Ca(OH)_2$. It is fed by a standard dry-feed mechanism into a slaking device, which is a large tank with tight-fitting cover and equipped with a dust- and vapor-removal unit. It is also equipped with a rotating mechanism or rake. Hot water may be supplied to the slaking mechanism in a ratio to the lime being fed that will give the appropriate temperature for complete slaking. The rake mechanism is so designed that there is some mechanical removal of the "grit" which comes from the calcining process. The grit may be either the clinkers from the powdered coal fuel or small particles of unburned limestone. Where large quantities of lime are used, the removal of this grit from the slaker and from the treatment basins may become a formidable problem. A recent development in the use of quicklime is what is called a "high-viscosity" slaker. This device has two multiblade mixers, and the lime-water ratio is adjusted to produce a slurry of approximately 35 per cent $Ca(OH)_2$. The blades of the two mixers are intermeshed with very small clearances. Particles of grit tend to lodge in these narrow spaces, stalling the mixer. However, a number of such machines have given satisfactory use.

The feeding of lime suspensions or slurries presents many problems. The slurries are very viscous and will clog any type of check valve or restricting mechanism. High-capacity rotameters will work if operated in a wide-open position. Valveless proportioning pumps have proved to be the most satisfactory method of metering lime slurries. The most effective way to transmit the lime slurry from the metering pump to the point of application is through a flexible hose. If the water used for slaking the lime has been softened, lined steel piping may be used. The diameter of the hose should be kept small so that the linear velocity of the slurry will be high. The flexible hose permits the crushing of any caking deposits and their removal from the line by flushing. The transmission of thin milk of lime suspension is subject to the same tendency to deposit calcium carbonate on the walls of the transmitting pipe or trough. Some installations use fixed piping, which is cleaned by periodic applications of strong chlorine solution. Other installations use larger-diameter rubber hoses which may be compressed to loosen the caking. Many installations ultimately resort to an open trough for the transmission of lime suspensions because of the ease with which they may be cleaned. The best solution is to have the point of application as close as possible to the slaker so that caking troubles are minimized.

It is emphasized again that care should be taken to avoid mixtures of alum and quicklime. This is because there is a tendency for the water of crystallization from the alum to start the slaking of the lime. In a closed container this may lead to a violent explosion. Equal care should be taken to avoid mixtures of ferric sulfate and lime. The hazards of handling lime are those of a fairly active chemical dust. Severe eye injuries or skin burns may result from contact with either quicklime or hydrated lime dust. The same thing is true to a lesser extent of the lime suspensions or slurries. Persons handling these materials should be adequately equipped with protective clothing, gloves, goggles, respirators, or face shields. Immediate treatment of lime burns is necessary to avoid prolonged discomfort.

Sodium Carbonate (Soda Ash). Soda ash, Na_2CO_3, used in the softening of water is a grayish white powder containing at least 98 per cent sodium carbonate (see AWWA Standard B201-59). It may be shipped in bulk or in bags or barrels. It is noncorrosive and may be stored in ordinary steel or concrete bins or silos. It may be fed in the conventional chemical dry feeder. Its solution may be transmitted through conventional pipelines or troughs. Its hazards are primarily those of a chemical dust. Protective clothing and devices such as gloves, respirators, goggles, etc., should be provided.

Sodium Chloride. The *AWWA Standards for Sodium Chloride* (AWWA Standard B200-69) require that the materials be homogeneous and in a dry granular form, white to grayish white or pink, brown, or brownish white in color. The size requirements state that rock salt should be of such fineness that it passes a No. 3 sieve, and 95 per cent of it should be retained on a No. 7 sieve. Evaporated salt should be of such fineness that at least 85 per cent should be retained on a No. 7 sieve. The material should dissolve rapidly without packing. The solution formed by dissolving the salt in distilled water should have a phenolphthalein alkalinity of zero and a hydrogen-ion concentration (pH) no higher than 8.0. Sodium chloride is available in bulk, in bags, or in other bulk containers as specified. Sodium chloride has a tendency to absorb moisture and to cake under certain conditions. Care should be taken to protect it from moisture in storage. (It is best stored in concrete bins.) It is highly soluble in water and may readily be made up to a desired concentration. It may be fed by a standard liquid chemical metering device. The solution may be transmitted through rubber or bronze lines. Exposure of the skin to large amounts of the dry salt would have a tendency to cause dehydration of the skin. Protective clothing and devices such as gloves and face shields should be provided.

MISCELLANEOUS

Copper Sulfate. Copper sulfate, $CuSO_4 \cdot 5H_2O$, is available in blue crystals or blue crystalline granules or powder. It is available in paper sacks or drums. It is used in the control of algae in impounding reservoirs. It is sometimes applied as a powder which is distributed by dusting with a suitable mechanism on the surface of the water. Another technique is to drag burlap bags of the crystals through the water, effecting solution and distribution by the same motion. Still another method of application is to meter the copper sulfate solution into a narrow control channel at the entrance to the impounding reservoir. This chemical and its solution are poisonous and corrosive. The solution may be kept in glass or rubber-lined containers and transmitted through noncorrosive lines. The solution is usually made up in batch form in a definite concentration and distributed as needed.

Sodium Bichromate. Sodium bichromate is a yellow crystalline solid, red or red-orange in color. Highly soluble in water, it is used as a corrosion inhibitor in certain nonpotable water systems. Its solution is quite corrosive and should be kept in noncorrosive containers and applied to noncorrosive lines. The powder is an extremely harmful dust. Adequate protective clothing, goggles, respirators, and/or face shields should be provided. The skin should be washed thoroughly after contact. It is very poisonous material and ingestion should be avoided.

The characteristics of chemicals discussed in this chapter are given in Table 17-3.

APPENDIX

Compressed-gas Shipping Containers

Classified by the Department of Transportation and the U.S. Coast Guard as nonflammable compressed gases, ammonia, chlorine, and sulfur dioxide must be packaged in containers that comply with DOT and/or Coast Guard regulations regarding loading, handling, and labeling when shipped in the United States by rail, water, or highway. State, local, and insurance requirements must also be adhered to. DOT regulations limit the maximum filling capacity of all compressed-gas containers (i.e., the per cent ratio of the weight of the gas in the container to the weight of water that the container will hold): for chlorine and sulfur dioxide containers, this limit is 125 per cent (approximately 88 per cent of total container volume); for ammonia containers, it varies between 50 and 57 per cent, depending upon the type of container. A variety of containers are available to meet individual customer needs; all containers are steel, are often equipped with one or more safety devices; and are pressure-tested at regular, specified intervals.

Cylinders. Cylinders are seamless bottles forged from one piece of steel. Those most popularly employed in waterworks practice have a commodity capacity of 100 or 150 lb, but many other sizes are available.

Regulations limit the maximum filling of chlorine cylinders at 150 lb and permit only one opening in the cylinder—the valve connection at the top. All chlorine cylinders must contain a fusible metal safety device

TABLE 17–3 Chemicals Used in Water Treatment

Chemical name and formula	Common or trade name	Shipping containers	Suitable handling materials	Available forms	Weight, lb cu ft	Solubility, lb gal	Commercial strength	Characteristics
Coagulation								
Aluminum sulfate $Al_2(SO_4)_3 \cdot 14H_2O$	Alum, filter alum, sulfate of alumina	100-, 200-lb bags, 300-, 400-lb bbls, bulk (carloads)	Dry—iron, steel; solution—lead-lined rubber, silicon, asphalt, 316 stainless steel	Ivory-colored: Powder Granule Lump	 38–45 60–63 62–67	4.2 (60 °F)	15–22% Al_2O_3	pH of 1% solution, 3.4
Ammonium aluminum sulfate $Al_2(SO_4)_3(NH_4)_2SO_4 \cdot 24H_2O$	Ammonia alum, crystal alum	Bags, bbls, bulk	Duriron, lead, rubber, silicon, iron, stoneware	Lump Nut Pea Powdered	64–68 62 65 60	0.3 (32 °F), 8.3 (212 °F)	11% AL_2O_3	pH of 1% solution, 3.5
Bentonite	Colloidal clay, volclay, wilkinite	100-lb bags, bulk	Iron, steel	Powder, pellet, mixed sizes	60	Insoluble (colloidal sol used)		
Ferric chloride* (a) $FeCl_3$ (35–45% solution)	"Ferrichlor," chloride of iron	5-, 13-gal carboys; trucks, tank cars	Glass, rubber, stoneware, synthetic resins	Dark brown syrupy liquid		Complete	37–47% $FeCl_3$, 20–21% Fe	
(b) $FeCl_3 \cdot 6H_2O$	Crystal ferric chloride	300-lb bbls		Yellow-brown lump			59–61% $FeCl_3$, 20–21% Fe	Hygroscopic (store lumps and powder in tight containers); no dry feed; optimum pH, 4.0–11.0
(c) $FeCl_3$	Anhydrous ferric chloride	500-lb casks, 100-, 300-, 400-lb kegs		Green-black powder			98% $FeCl_3$, 34% Fe	
Ferric sulfate* $Fe_2(SO_4)_3 \cdot 9H_2O$	"Ferriflor," Ferrisul	100-, 175-lb bags, 400-, 425-lb drums	Ceramics, lead, plastic, rubber, 18–8 stainless steel	Red-brown powder 70 or granule 72		Soluble in 2–4 parts cold water	90–94% $Fe_2(SO_4)_3$, 25–26% Fe	Mildly hygroscopic; coagulant at pH 3.5–11.0
Ferrous sulfate* $FeSO_4 \cdot 7H_2O$	Copperas, green vitriol	Bags; bbls.; bulk	Asphalt, concrete, lead, tin, wood	Green crystal granule, lump	63–66	0.5 (32 °F), 1.0 (68 °F), 1.4 (86 °F)	55% $FeSO_4$, 20% Fe	Hygroscopic; cakes in storage; optimum pH, 8.5–11.0
Potassium aluminum sulfate, $K_2SO_4Al_2(SO_4)_3 \cdot 24H_2O$	Potash alum	Bags, lead-lined; bulk (carloads)	Lead, lead-lined, rubber, stoneware	Lump Granule Powder	62–67 60–65 60	3.0 (68 °F), 3.3 (86 °F)	10–11% Al_2O_3	Low, even solubility; pH of 1% solution, 3.5
Sodium aluminate, $Na_2OAl_2O_3$	Soda alum	100-, 150-lb bags, 250-, 440-lb drums; solution	Iron, plastics, rubber, steel	Brown powder, liquid (27 °Be)	50–60	Complete	70–80% $Na_2Al_2O_4$, min. 32% $Na_2Al_2O_4$	Hopper agitation required for dry feed
Sodium silicate, Na_2OSiO_2	Water glass	Drums; bulk (tank trucks, tank cars)	Cast iron, rubber, steel	Opaque, viscous liquid			38–42 °Bé	Variable ratio of Na_2O to SiO_2; pH of 1% solution, 12.3
Disinfection and dechlorinating agents								
Ammonium aluminum sulfate, $Al_2(SO_4)_3(NH_4)_2SO_4 \cdot 24H_2O$	Ammonia alum, crystal alum	Bags, bbls.; bulk	Duriron, lead, rubber, silicon, iron, stoneware	Lump Nut Pea	64–68 62 65	0.3 (32 °F), 8.3 (212 °F)	11% Al_2O_2	pH of 1% solution, 3.5

mmonium sulfate $NH_4)_2SO_4$*	Sulfate of ammonia	100-lb bags	Ceramics, plastics, rubber, iron (dry)	White or brown crystal		42.5	6.3 (68 °F)	Cakes in dry feed, add $CaSO_4$ for free flow
hydrous ammonia, H_3	Ammonia	50-, 100-, 150-lb cylinders, in bulk (tank cars and trucks)	Glass, iron, monel metal, nickel, steel	Colorless gas		3.9 (32 °F), 3.1 (60 °F) 1.8 (125 °F)	99–100% NH_3	
qua ammonia, H_4OH	Ammonia water, ammonium hydrate, ammonium hydroxide	Carboys, 750-lb drums, 8,000-gal tank cars or trucks	Glass, iron, monel metal, nickel, steel	Colorless liquid		Completely	29.4% NH_2 (26 °Bé)	
alcium hypochlo-te, $CaOCl_2$ H_2O	"HTH," Perchloron, "Pittchlor"	5-lb cans; 100-, 300-, 800-lb drums	Glass, rubber, stoneware, wood	White granule, powder	52.5		70% available Cl_2	1–3% available Cl_2 solution used
lorinated lime, CaO $CaOCl_2 \cdot 3H_2O$	Bleaching powder, chloride of lime	100-, 300-, 800-lb drums	Glass, rubber, stoneware, wood	White powder	48		25–37% available Cl_2	Deteriorates
hlorine, Cl_2	Chlorine gas, liquid chlorine	100-, 150-lb cylinders; 1-ton containers; 16-, 30-, 55-, 85-, and 90-ton tank cars; tank trucks (about 15–16 tons)	Dry—black iron copper, steel; wet gas—glass, hard rubber, silver	Liquefied gas under pressure	91.7	0.07 (60 °F), 0.04 (100 °F)	99.8% Cl_2	
hlorine dioxide, lO_2	Chlorine dioxide	Generated as used	Plastics, soft rubber (avoid hard rubber)	Yellow-red gas		0.02 (30 mm)	26.3% available Cl_2	
zone, O_3	Ozone	Generated at site of application	Aluminum, ceramics, iron, steel, wood	Colorless gas				
rosodium ulfite	Sodium metabisulfite	Bags; drums, bbls	Iron, steel, wood	White crystalline powder		Completely in water	Dry, 67% SO_2; sol., 33.3% SO_2	Sulfurous odor
dium chlorite, $aClO_2$	Technical sodium chlorite	100-lb drums	Metals (avoid cellulose materials)	Light orange powder, flake			82% $NaClO_2$, 30% available Cl_2	Generates ClO_2 at pH 3.0
dium hypochlo-ite, $aOCl$	Sodium hypochlorite	5-, 13-gal carboy 1,300–2,000-gal tank trucks	Ceramics, glass, plastics, rubber	Light yellow liquid			12–15% available Cl_2	
dium ulfite, a_2SO_3	Sulfite	Bags, drums, bbls.	Iron, steel, wood	White crystalline powder		Complete in water	23% SO_2	Sulfurous taste and odor
lfur lioxide, O_2	Sulfurous acid anhydride	Steel cylinders, ton containers, tank cars or trucks	Aluminum, brass, Durco D-10, stainless steel 316	Colorless gas		20% at 32 °F, complete in water	99% SO_2	Irritating gas
			Fluoridation and fluoride adjustment					
mmonium alico flouride, $NH_4)_2SiF_6$	Ammonium fluorsilicate	100- and 400-lb drums	Steel, iron, and lead	White crystals		1.7 (63 °F)	100%	White, free-flowing solid
alcium fluoride, CaF_2	Fluorspar	Bags; drums; bbls; hopper cars, trucks	Steel, iron, and lead	Powder		Very slight	85% CaF_2, less than 5% SiO_2	

or list of approved organic coagulant aids, see text.

TABLE 17-3 Chemicals Used in Water Treatment *(Continued)*

Chemical name and formula	Common or trade name	Shipping containers	Suitable handling materials	Available forms	Weight, lb/cu ft	Solubility, lb/gal	Commercial strength	Characteristics
Hydro-fluosilicic acid, H_2SiF_6	Fluosilicic acid	Rubber-lined drums, trucks; or R.R. tank cars	Rubber-lined steel, PVC	Liquid		Approx. 1.2 (65 °F)	Approx. 35%	
Hydrogen fluoride, HF	Hydrofluoric acid	Steel drums; tank cars	Steel	Liquid			70%	Below 60%, steel cannot be used
Sodium fluoride,* NaF	Fluoride	Bags; bbls.; fiber; drums kegs	Iron, lead, steel	Nile blue or white powder: Light Dense	 50 75	0.35 (most temps.)	90–95% NaF	pH of 4% solution, 6.6
Sodium silico fluoride, Na_2SiF_6	Sodium silicofluoride	Bags; bbls.; fiber, drums	Iron, lead, steel	Nile blue or yellowish-white powder	72	0.03 (32 °F), 0.06 (72 °F), 0.12 (140 °F)	99% Na_2SiF_6	pH of 1% solution, 5.3
Fluoride adjustment								
Aluminum oxide, Al_2O_3	Activated alumina	Bags; drums	Iron, steel, lead	Powder, granules (up to 1½ in. diam)	Variable	Insoluble	100%	
Bone charcoal	"Fluo-Carb"	Bags; drums, bulk	Wood, iron, steel	Granules	Variable			Black; best used in beds for presolution
Tricalcium phosphate	"Fluorex"	Bags; drums, bulk, bbls.	Iron, steel	Granular, technical	50–63	Insoluble		Also available as white powder
High-magnesium lime	Dolomitic lime	Bags; bbls., bulk	Wood, iron, steel	Lump, pebble, ground		Slakes slowly	58% CaO, 40% MgO_2	
Stabilization and corrosion control								
Disodium phosphate, $Na_2HPO_4 \cdot 12H_2O$	Basic sodium phosphate, DSP, secondary sodium phosphate	125-lb kegs, 200-lb bags, 325-lb bbls	Cast iron, steel	Crystal	60–64	0.4 (32 °F), 6.4 (86 °F)	19.5% P_2O_5	Precipitates Ca, Mg; pH of 1% solution, 9.1
Sodium hexametaphosphate, $(NaPO_3)_6$	"Calgon," glassy phosphate, vitreous phosphate	100-lb bags	Hard rubber, plastics, stainless steel	Crystal, flake, powder	47	1–4.2	66% P_2O_5 (unadjusted)	pH of 0.25% solution, 6.0–8.3
Sodium hydroxide, NaOH	Caustic soda, soda, lye	100-, 700-lb drums; bulk (trucks, tank-cars)	Cast iron, rubber, steel	Flake Lump Liquid		2.4 (32 °F), 4.4 (68 °F), 4.8 (104 °F)	98.9% NaOH, 74–76% NaO_2	Solid; hygroscopic; pH of 1% solution, 12.9
Sulfuric acid, H_2SO_4	Oil of vitriol, vitriol	Bottles, carboys, drums; trucks, tank cars	Concentrated—iron, steel, dilute—glass, lead, porcelain, rubber	Solution (60–66 °Bé)		Complete	77.7% H_2SO_4 (60 °Be); 93.2% H_2SO_4 (66 °Be)	Approx. pH of 0.5% solution, 1.2
Tetrasodium pyrophosphate, $Na_4P_2O_7 \cdot 10H_2O$	Alkaline sodium pyrophosphate, TSPP	125-lb kegs, 200-lb bags, 300-lb bbls.	Cast iron, steel	White powder	68	0.6 (80 °F), 3.3 (212 °F)	53% P_2O_5	pH of 1% solution, 10.8
Trisodium phosphate, $Na_3PO_4 \cdot 12H_2O$	Normal sodium phosphate, tertiary sodium phosphate, TSP	125-lb kegs, 200-lb bags, 325-lb bbls	Cast iron, steel	Crystal: Coarse Medium Standard	 56 58 61	0.1 (32 °F), 13.0 (158 °F)	19% P_2O_5	pH of 1% solution, 11.9

				Softening				
Calcium hydroxide, $Ca(OH)_2$	Hydrated lime, slaked lime	50-lb bags; 100-lb bbls.; bulk (carloads) trucks	Asphalt, cement, iron, rubber, steel	White powder Light Dense		0.014 (68 °F) 0.012 (90 °F)	85–99% $Ca(OH)_2$, 63–73% CaO	Hopper agitation required for dry feed of light form
Calcium oxide,* CaO	Burnt lime, chemical lime, quick-lime, unslaked lime	50-lb bags; 100-lb bbls.; bulk (carloads)	Asphalt, cement, iron, rubber, steel	Lump, pebble, granule.		Slakes to form hydrated lime	75–99% CaO	pH of saturated solution, 12.4; detention time, temperature, amount of water all critical for efficient slaking
Sodium carbonate, Na_2CO_3	Soda ash	Bags; bbls.; bulk (carloads, trucks)	Iron, rubber, steel	White powder Extra light Light Dense	 23 35 65	1.5 (68 °F), 2.3 (86 °F)	99.4% Na_2CO_3, 58% Na_2O	Hopper agitation required for dry feed of light and extra-light forms; pH of 1% solution, 11.3
Sodium chloride,* NaCl	Common salt, salt	Bags; bbls.; bulk (carloads)	Bronze, cement, rubber	Rock fine		2.9 (32 °F), 3.0 (68 °F), 86 °F	98% NaCl	
				Taste and odor control				
Activated carbon,* C	"Aqua Nuchar," "Hydrodarco," "Norite"	Bags, bulk	Dry—iron, steel; wet—rubber, silicon, iron, stainless steel	Black granules powder	15	Insoluble (suspension used)		
Chlorine, Cl_2	Chlorine gas, liquid chlorine	100–150-lb cylinders, 1-ton tanks, 16-, 30-, 55-ton tank cars	Dry—black iron, copper, steel; wet gas—glass, hard rubber, silver	Liquefied gas under pressure	91.7	0.07 (60 °F), 0.04 (100 °F)	99.8% Cl2	
Chlorine dioxide, ClO_2	Chlorine dioxide	Generated as used	Plastics, soft rubber (avoid hard rubber)	Yellow-red gas		0.02 (30 mm)	26.3% Available Cl_2	
Copper sulfate,* $CuSO_4 \cdot 5H_2O$	Blue vitriol, blue stone	100-lb bags; 450-lb bbls.; drums	Asphalt, silicon, iron, stainless steel	Crystal Lump Powder	75–90 73–80 60–64	1.6 (32 °F), 2.2 (68 °F), 2.6 (86 °F)	99% $CuSO_4$	
Ozone, O_3	Ozone	Generated at site of application	Aluminum, ceramics glass	Colorless gas				
Potassium permanganate, $KMnO_4$	Purple salt	Bulk, bbls., drums	Iron, steel, wood	Purple crystals		Infinite	100%	Danger of explosion on contact with organic matters

*For list of approved organic coagulant aids, see text designed to melt at between 158 and 165 °F; an integral part of the standard operating valve, one type has fusible metal cast directly into a threaded hole in the valve body, while another type has a threaded bronze plug containing the fusible metal which is screwed into a tapped hole in the valve body. This safety device releases the container contents and prevents hydrostatic failure from excessive pressure attendant on exposure of the container to fire or other excessive heat. Chlorine cylinders filled to the maximum legal limit become completely liquid-full at 154 °F. Cylinders of 100-lb capacity vary in diameter from 8¼ to 10¼ in., in height from about 40 to 59 in., and have an empty weight from about 63 to 115 lb. Cylinders of 150-lb capacity vary in diameter from 10¼ to 10¾ in., in height from about 53 to 56 in., and have an empty weight from about 85 to 140 lb.

Ammonia cylinders appear bulky in comparison with chlorine and sulfur dioxide cylinders because the density of ammonia (38.50 lb per cubic foot at 60 °F) is scarcely half that of chlorine (88.79 at 60 °F) and that of sulfur dioxide (87.03 at 60 °F). Cylinders containing less than 165 lb ammonia are not required to be equipped with a safety device. Cylinders filled to the maximum legal limit become completely liquid-full at about 145 °F. Two types of cylinders are in current use: tubes and bottles.

The operating valve on ammonia cylinders is connected to a dip tube positioned in such a way that either gas or liquid ammonia can be emptied from the container. Tube types of 100-lb capacity have a diameter of about 10 in., are about 86 in. long, and have an average empty weight of about 170 lb; those of 150-lb capacity have a diameter of about 12 in., are about 86 in. long, and have an average empty weight of 240 lb. Bottle types of 100-lb capacity have a diameter of about 12¼ in., a length of 55 to 57 in., and an empty weight varying from 90 to 135 lb.; those of 150-lb capacity have a diameter of about 14¾ in., a length of 56 to 58 in., and vary in empty weight from about 140 to 200 lb. Containers of 50-lb capacity, both tube and bottle types, also are frequently used.

Sulfur dioxide cylinders of 70-lb capacity contain two safety devices designed to melt at about 165° F; one, as in chlorine cylinders, an integral part of the operating valve and the other at the bottom of the cylinder. Some cylinders have a riser or dip tube attached to the valve and extending to the bottom of the cylinder allowing liquid withdrawal with the cylinder remaining in an upright position. Cylinders of 100-lb capacity have a diameter of about 10¼ in., a length of about 35½ in., and an empty weight of about 55 lb.; those of 150-lb capacity vary in diameter from 10¼ to 12¼ in., in height from 35½ to 50 in., and have an empty weight of about 70 lb.

Regulations permit shipment of chlorine, ammonia, and sulfur dioxide cylinders by rail in either carload or less-than-carload lots. Shipments by motor vehicles are also permitted in less-than-carload lots or in truckload quantities of various minimum weights depending upon the motor carrier and area of transportation.

Ton Containers. Ton containers for chlorine, ammonia, and sulfur dioxide are welded cylindrical steel tanks usually having convex-inward heads and sides crimped inward to form chimes which provide a substantial grip for lifting containers. (Some older containers have compound curvature of one end.) Contemporary containers are usually equipped with six fusible metal plugs, three in each and located 120° apart. They also are equipped with two operating valves at one end, each of which is connected inside the container to an eduction pipe terminating near the side wall. These containers, having a diameter of about 30 in. and an average length of about 80 in., vary in empty weight from about 1,300 to 1,600 lb. (DOT regulations also permit a somewhat lighter ton container of different design for sulfur dioxide service.) They are filled with about 2,000 lb each of chlorine and sulfur dioxide and 800 lb of anhydrous ammonia.

Chlorine, ammonia, and sulfur dioxide ton containers are authorized for railroad shipment, but only on a special tank-car frame known as a "multiunit tank car." This car is designed to hold 15 containers. The initial rail shipment of these containers is unloaded from the car at the consumer's plant. In subsequent shipments the full containers are exchanged for empties returned for refilling. (No freight is charged on the return carload of empty containers since tank cars are entitled to free return movement.) It is impractical to ship fewer than 15 containers because the rail transportation fee is figured for 15 full containers at prevailing carload rates. TMU cars must be consigned for delivery and unloading on a *private* track; where a private track is not available, the containers may be removed from the car frame on carrier tracks if proper written permission is first obtained. Regulations also provide that one or more ton containers may be transported on trucks or semitrailers provided they are securely chocked or clamped and provided adequate transfer facilities are available when container transfer in transit is necessary.

Other Shipping Containers. DOT regulations permit shipment of compressed gases in a variety of other containers such as tank cars (rail), tank trucks, and portable tanks (water capacity not exceeding 1,000 lb and designed to be temporarily attached to a motor vehicle, other vehicle, railroad car other than tank car, or vessels). Except for chlorine, quantities consumed in normal waterworks practice do not often warrant consideration of these containers.

Single-unit chlorine tank cars, which by regulation must be unloaded on a private track, are available in 16-, 30-, 55-, 85-, and 90-ton capacities. These containers, unlike cylinders and ton containers, are designed to be unloaded as liquid which must be vaporized to gas where process requirements so indicate; in a few instances they are unloaded into stationary storage tanks. Large consumers along waterways might choose to consider barge chlorine shipments; those consumers having no private track facilities and not immediately adjacent to suitable waterways might choose to consider tank-truck shipments. In both cases, if such shipments can be provided, transfer of container contents to stationary storage tanks is necessary.

Handling Compressed-gas Shipping Containers

Various mechanical devices such as skids, troughs, and up-ending cradles facilitate handling of compressed-gas cylinders. When unloading from trucks or platforms, cylinders must not be dropped to ground level. If cylinders must be lifted and an elevator is not available, specially designed cradles or carrying platforms in combination with a crane or derrick are recommended; chains, lifting magnets, and rope slings which encircle the cylinders are unsafe and should not be used. For lateral movements a properly balanced handtruck is useful. Cylinders being moved should always have valve-protection hoods in place; these hoods are not designed to hold the weight of cylinders and their contents, and cylinders should never be lifted by this means.

Ton containers may be moved by various means, such as by specially fitted trucks and dollies, by a monorail system, and by rolling. Where it is necessary to lift them, such as from a multiunit car or truck, a suitable lift clamp in combination with a hoist or crane of at least 2 tons capacity should be used. Valve-protection hoods should always be in place when moving ton containers.

Receiving and unloading areas and safety precautions applicable to handling single-unit railroad tank cars, tank trucks, and other shipping containers are subject to strict regulations.

Storing Compressed-gas Shipping Containers

Cylinders of anhydrous ammonia, chlorine, and sulfur dioxide should preferably be stored upright and secured in a manner that permits ready access and removal. Ton containers should be stored horizontally, slightly elevated from ground or floor level and blocked to prevent rolling; a convenient storage rack is obtained by supporting both ends of containers on rails or I beams. Ton containers should not be stacked or racked more than one high unless special provision is made for easy access and removal. Full and empty cylinders and ton containers should be segregated.

Storage areas should be clean, cool, well ventilated, and protected from corrosive vapors and continual dampness. Cylinders and ton containers stored indoors should be in a fire-resistant building, away from heat sources (such as radiators, steam pipes, etc.), flammable substances, and other compressed gases. Subsurface storage areas should be avoided, especially for chlorine and sulfur dioxide. If natural ventilation is inadequate, storage and use areas should be equipped with suitable mechanical ventilators. Mechanical ventilation schemes for chlorine and sulfur dioxide are similar, both gases being considerably heavier than air; because ammonia is lighter than air, it requires different ventilation schemes. Cylinders and ton containers stored outdoors should be shielded from direct sunlight and protected from accumulations of rain, ice, and snow.

All storage, handling, and use areas should be of such design that personnel can quickly escape in emergencies. It is generally desirable to provide at least two means of exit. Doors should open out and lead to outside galleries or platforms, fire escapes, or other unobstructed areaways.

Emptying Compressed-gas Containers

Chlorine and ordinary sulfur dioxide cylinders deliver gas when in an upright position and liquid when in an inverted (or partially so) position. Bottle- and tube-type ammonia cylinders can deliver gas in either an upright or, if the dip tube is properly positioned, in a horizontal position. Ton containers in a horizontal position with the two valves in a vertical line deliver gas from the upper valve and liquid from the lower valve.

To withdraw gas from a compressed-gas cylinder or ton container, the liquid form of the material must be vaporized. The flow rate is a function of the vaporization rate which, in turn, is dependent on the rate of heat transfer to the liquid.

The dependable, continuous discharge rate of chlorine gas from a 100- or 150-lb cylinder, at about 70 °F under normal circulation conditions and without sweating, is about 1¾ lb per hour against a 35-psi back pressure. Under similar conditions, the gas discharge rate from a ton container is about 15 lb per hour. If sweating can be tolerated, these rates can be doubled; for short periods they may be greatly exceeded. Heat must never be applied to any type of chlorine container in an effort to increase the vaporization and, hence, discharge rates. If the gas discharge rate from a single chlorine cylinder or ton container is inadequate, two or more can be connected to a manifold and discharged simultaneously. A scale should be provided, as this is the most accurate means of determining container contents. Some water plants operate without scales. The dependable, continuous discharge rate of liquid chlorine, at about 70°F and against a 35-psi back pressure, is about 200 lb per hour for cylinders and 400 lb per hour for ton containers. Batch discharge rates may be considerably higher. Connection of cylinders or ton containers discharging liquid chlorine to a manifold is *not* recommended. (A common practice is to connect the two or three ton containers on a scale to a common discharge header.)

Emptying of single-unit chlorine tank cars should be accomplished through a suitable metal flexible connection to accommodate the rise of the car as its springs decompress. These cars almost invariably are emptied by discharging liquid. The liquid chlorine may be unloaded by its own vapor pressure. Cold weather usually decreases the unloading rate; in extremely cold climates it may be helpful to unload cars in a shed maintained at about 70°F. If necessary, the car pressure can be increased by padding, sometimes done by the tank car loader. Alternatively, on-site facilities might be provided for by adding clean, dry air to the car. Vaporizers must be used when the consuming process requires gas.

In general, requirements for emptying chlorine tank trucks and barges are similar to those for emptying tank cars. Suitable chlorine bulk storage facilities are also required. In the case of barges piping, loading, and unloading arrangements must be approved in the United States by the Coast Guard. Where bulk storage is indicated (e.g., when chlorine is shipped by barge or, in most cases, by tank truck) a sufficient pressure differential must be maintained between the shipping container and the storage container. Facilities must be provided to vent chlorine gas or chlorine-air mixtures from the storage tank to the consuming process or other disposal system; venting may be required during the entire unloading period. When transferring chlorine from the storage tank to the consuming process, air padding may be necessary. The procedure is essentially the same as that required for emptying tank cars. Reliable means must be provided for determining tank contents; weight measuring devices are preferred and gage glasses should not be used. Especially where night operations are contemplated, adequate lighting, including auxiliary sources, is essential. Storage tanks should be of such number and capacity as is consistent with the size of shipments received and rate of consumption. A thorough investigation of all pertinent regulations and insurance restrictions regarding their design, capacity, and location should be made prior to beginning construction.

Either bottle- or tube-type ammonia cylinders of 150-lb capacity, standing vertically, will usually deliver up to about 30 cu ft gas per hour. The same cylinders racked horizontally (requiring more space) each will yield about 40 to 50 cu ft gas per hour. When the demand is such that ammonia can only be supplied by several cylinders simultaneously delivering gas, manifolding facilities might have to be provided. Cylinders may be manifolded standing vertically or placed horizontally in a wall rack: tube types are usually placed horizontally. At least one standby cylinder should also be provided where continuous operation is necessary. Where the demand is excessive, the system is usually designed to withdraw liquid from one cylinder and vaporize it in a steam- or electric-heated evaporator. Where continuous flow is required, it is customary to have at least two cylinders connected, but only one in use at any time. Scales are usually necessary for large installations.

Anhydrous ammonia ton containers and portable tanks can be emptied in a manner similar to that for cylinders. For emptying in the liquid phase, a compressor or liquid pump frequently is employed. Cargo tanks are almost invariably emptied as liquid ammonia (because gas unloading would require a longer-than-practicable detaining time) by use of a liquid pump or a vapor compressor similar to single-unit tank cars. Storage facilities are required. Single-unit tank cars are unloaded into a receiving or storage tank using a vapor compressor, a steam vaporizer, or a liquid pump. Suitable unloading lines and other appurtenances are required, depending on the unloading scheme employed. (The storage tanks are usually equipped with gages that show the per cent of liquid storage.)

A 150-lb sulfur dioxide cylinder will deliver about 2 lb per hour gas. A ton container at 70 °F and at the corresponding pressure (35 psi) and with 10 psi pressure on the control valve feeding a reaction tank will deliver about 25 lb per hour gas. Under similar conditions, a 150-lb cylinder will deliver about 5 lb per minute, and a ton container will deliver about 300 lb per hour liquid sulfur dioxide. Unless the gas requirements are small, manifold arrangements may be indicated, or provision might be necessary for the container to acquire heat from some external source other than the surrounding atmosphere. Where gas requirements are very large, containers should be emptied as liquid, which can subsequently be gasified by supplying heat in electrically or steam-heated vaporizers. To withdraw liquid, a pressure differential must be maintained; a variety of means can be devised to attain this situation. Where sulfur dioxide containers are heated to promote discharge, great care should be exercised to prevent containers from reaching a temperature exceeding 125 °F. Cylinders can be heated in a number of ways: electric strip heaters clamped to the cylinder and fitted with a thermostat set to turn on or off at no more than 100 °F; a steam coil placed against the cylinder; or a warm liquid bath covering not more than the lower half of the cylinder are all suitable. Open flames or blowtorches must not be used. A satisfactory method of heating ton containers is to employ a small, heated and well-insulated wooden structure that accommodates one or two containers. A common method of heating is with steam pipes placed on the floor of the structure directly below the container, the temperature being automatically controlled by a thermoregulating valve on the steam line. Thermostatically controlled strip heaters also are suitable.

Engineering Control of Hazards

Careful consideration should be given to methods of handling shipping containers, especially those containing compressed gases, oxidants, and corrosive materials. Height of ceilings for overhead hoists and floors of sufficient construction for ease in handling mechanical equipment should be provided. Storage and use areas should be properly ventilated so as to minimize possible accidental reaction of chemicals involved based on their characteristics previously noted. Piping systems should be as simple as possible with a minimum number of joints; they should be well supported, protected against temperature extremes, and adequately sloped to allow proper drainage.

Long pipelines for liquid chlorine should be avoided. Sections of pipelines that can be isolated or shut off at both ends (such as by valves) must be provided with a suitable expansion chamber to avoid possible hydrostatic rupture due to pressure and volume increases accompanying high temperatures. Condensation or reliquefaction can occur in chlorine gas lines which pass through areas where the temperature is below the temperature-pressure equilibrium indicated on the chlorine vapor pressure curve (Fig. 4). It can be prevented by supplying properly controlled heat or by reducing the pressure. The temperature of chlorine containers and gas pipelines should be lower than the temperature of the chlorinator to prevent condensation; if chlorine gas condenses, the chlorine will be reliquefied and result in erratic chlorinator operation. Chlorine pipelines removed from service for even very brief periods should be closed in a suitable manner to preclude the entrance of moisture which will cause serious corrosion problems.

Equipment cleaning and repairs should be performed under the direction of thoroughly trained personnel who are fully familiar with all of the hazards and the safeguards necessary for the safe performance of the work. All precautions pertaining to education, protective equipment, and health and fire hazards should be reviewed and understood. Repairs on chlorine systems should not be undertaken while the system is in operation and when piping systems are in service. Chlorine pipelines and equipment should be first purged with *dry* air as a safeguard to health; this is especially important where cutting or welding operations are undertaken, because iron and steel will ignite in chlorine at about 450 °F. Immediate drying of a chlorine pipeline into which water or moisture has been introduced or which has been opened for repairs is essential if corrosion is to be prevented.

The technical problems of designing storage and use areas, equipment, and piping systems, providing adequate ventilation, and formulating operating procedures which ensure maximum security and economy can best be handled by experienced engineers and safety and fire-protection specialists. Assistance and literature are available from such organizations as the Chlorine Institute, Inc., the Compressed Gas Association, the Manufacturing Chemists' Association, and from material and equipment producers and suppliers.

Some additional precautions, recommendations, and safety practices regarding handling and use of hazardous chlorination chemicals are outlined in the AWWA's *Safety Practice for Water Utilities* and the Water Pollution Control Federation's *Safety in Wastewater Works* manuals.

Emergency Measures

As soon as there is indication of a leak of a compressed gas or other abnormal condition, steps should be taken to correct it. Leaks never get better by themselves; they *always* get worse if not promptly and suitably corrected. If the material is a hazardous one, authorized, trained personnel with suitable gas masks should investigate, and all other persons should be kept away from the affected area. The ventilation system should be placed in operation immediately. Unconfined chlorine and sulfur dioxide, being heavier than air, tend to lie close to ground level; ammonia, on the other hand, being lighter than air, tends to rise to upper levels. (These characteristics must be kept in mind in designing chemical storage and use areas and appropriate natural or mechanical ventilation systems.) If leaks cannot be handled promptly, the chemical supplier or nearest office or plant of the producer should be called immediately for emergency assistance.

In case of fire, containers should be removed from the fire zone immediately. Portable tanks, tank cars, trucks, and barges should be disconnected and, if possible, also moved from the fire zone. *If there are no leaks* water should be applied to cool compressed gas containers. Water must never be applied, however, to a leaking chlorine or sulfur dioxide container. These chemicals are only slightly soluble in water and the corrosive character of their reaction with water *always* will intensify the leak. In addition, the heat supplied by even cold water will increase the vaporization rate. Leaking chlorine or sulfur dioxide containers similarly should not be thrown into a body of water because the leak will be aggravated and the container might float when still partially full, allowing uncontrolled gas evolution at the surface. Leaks involving ammonia, on the other hand, can be readily controlled with water; indeed water sprays and sprinkling systems might well be provided for controlling serious ammonia leaks.

If a leak occurs in equipment or piping, the supply should be discontinued, and the material under pressure at the leak should be disposed of. Leaks around container-valve stems usually can be stopped by tightening the packing nut or gland. If this does not stop the leak, the container valve should be closed and material under pressure in the outlet piping should be disposed of. If the valve does not shut off tight, the outlet plug or cap should be applied. In the case of a leaking valve of a ton container, the container should be positioned so that the valves are in a vertical plane with the leaky valve on top.

If confronted with other container leaks, one or more of the following should be considered:

1. Position cylinders or ton containers so that gas instead of liquid escapes. The containers may be insulated with sacks, earth, etc., to decrease absorption of heat and the discharge rate.
2. Apply appropriate emergency kit capping devices, if available.
3. Call the supplier or nearest producer for emergency assistance.
4. If practical, reduce pressure in the container by removing the gas to process or a suitable disposal system. Caustic soda, soda ash, or another suitable alkali absorption system should be provided for disposing of chlorine and sulfur dioxide from leaking cylinders and ton containers. (100 lb of SO_2 can be neutralized with 150 lb caustic soda; 100 lb Cl_2 can be neutralized with 125 lb caustic soda. Ten gallons of water should be used to dissolve each 25 lb of caustic soda.) Ammonia can be readily dissolved in water.
5. In some cases it might be desirable and possible to move the container to an isolated spot where it will do the least harm.

Finding Leaks. The characteristic odors of ammonia, chlorine, and sulfur dioxide provide warning of leaks. Moistened phenolphthalein paper becomes pink in the presence of ammonia, and a supply of this indicator paper should be available. Chlorine and sulfur dioxide react with ammonia to form dense white fumes; a supply of strong ammonia water (commercial 26°Bé, as household ammonia is not sufficiently strong) should be available for locating leaks. The leak can be readily detected by holding an ammonia-saturated cloth near the suspected area. Compressed gas containers (in storage and use), piping, and equipment should be tested for leaks daily.

Employee Protective Equipment

Severe exposure and potential health hazards exist wherever noxious compressed gas and other respiratory irritants are handled or used. A suitable gas mask should be provided for every employee involved with their handling or use. Additionally, suitable protective equipment for emergency use should be available outside of rooms where hazardous materials are located, near the entrance, away from areas of likely contamination. Such equipment might be provided in several locations at larger installations. Only respiratory protective equipment approved by the U.S. Bureau of Mines specifically for chlorine service, ammonia service, or sulfur dioxide service may be used.

Canister-type gas masks with a full facepiece and specific or all-purpose commodity canister should be used only for relatively short exposure periods and only if it has been clearly established that sufficient oxygen is present (not less than 16 per cent in air) and that contamination does not exceed the allowable level (1 per cent for chlorine, 2 per cent for sulfur dioxide, 3 per cent for ammonia). Canister masks might not be useful in emergencies, since these criteria might not be readily ascertained, especially if suitable forced-ventilation schemes are not provided. Regular replacement of overage canisters, even though unused, is recommended.

Self-contained breathing apparatus with a full facepiece and a cylinder of air or oxygen carried on the body or with a canister that produces oxygen chemically is suitable for high contaminant concentrations and is the preferred means of respiratory protection. It provides protection for a period which varies with the amount of air, oxygen, or oxygen-producing chemicals carried.

Positive-pressure (blower) hose masks, compressed-air line masks, or combination compressed-air line mask and self-contained breathing apparatus are also suitable provided the mask and accessories have been approved by the U.S. Bureau of Mines.

Employee Training

Safety in handling hazardous materials depends, to a great extent, upon the effectiveness of employee education, proper safety instructions, intelligent supervision, and the use of safe equipment. Training for both new and old employees should be conducted periodically to maintain a high degree of safety in handling procedures. Employees should be thoroughly informed of the hazards that may result from improper handling. They should be cautioned to prevent leaks and thoroughly instructed regarding proper action to take in case they occur. Each employee should know what to do in an emergency and should be fully informed as to first-aid measures.

In addition, employee training should encompass the following:

1. Instruction and periodic drill or quiz regarding the locations, purpose, and the use of emergency fire-fighting equipment, alarms, and emergency crash shut-down equipment such as valves and switches.

2. Instruction and periodic drill or quiz regarding the locations, purpose, and use of personal protective equipment.
3. Instruction and periodic drill or quiz regarding the locations, purpose, and use of safety showers, eye baths, bubbler drinking fountains, or the closest source of water for use in emergencies.
4. Instruction and periodic drill or quiz of selected employees regarding the locations, purpose, and use of respiratory first-aid equipment.
5. Instruction to avoid inhalation of toxic vapors and all direct contact with corrosive liquids.
6. Instruction to report to the proper authority all leaks and equipment failures.

Respiratory protective equipment should be carefully maintained, inspected, and cleaned after each use and at regular intervals. Defective or inoperable equipment is worse than none at all. All equipment should be used and maintained in strict accord with the manufacturer's instructions. No person should enter contaminated areas unless attended by an observer who can rescue him in event of respirator failure or other emergencies.

It is good practice to provide eye-protection devices (or masks with full facepieces) and other suitable protective clothing to workers exposed to hazardous materials. Emergency showers, eye baths, or other suitable waterflush systems should be provided in convenient locations for use by accidentally exposed personnel.

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18

Saline Water Conversion

By WILLIAM E. KATZ and ROLF ELIASSEN

SALINE AND BRACKISH WATERS AS WATER SOURCES

Water utilities have traditionally obtained water supplies from "fresh" water sources through civil or mechanical works, e.g., dams, aqueducts, pipelines, wells, pumps, filters, and settling basins. Over the past century, mechanical and chemical treatment methods have been developed to remove from freshwater such common impurities as bacteria, turbidity, color, tastes, odors, iron, or hardness. Most of the earth's water, however, is saline—rather than fresh—and contains impurities which could not, until recently, be economically removed by available treatment processes. This chapter deals with new thermal, electrical, physical, and chemical processes which have been and are being developed to treat saline and brackish waters by removing such dissolved impurities.

Only about 0.6 per cent of the 326 million cubic miles of total water found on earth is on the land, while 99.4 per cent is in the seas and polar ice caps.[1] Of the 2 million cubic miles of "land" water, about one-half is in the first half-mile of the crust of the earth and an almost equal amount in the next mile and a half. Only about 1 per cent of the land water is in freshwater lakes, an equal amount in saline lakes, about 0.1 per cent in all rivers, and less than 0.001 per cent in the atmosphere at any one time. A significant percentage of the groundwater is highly mineralized, and such water is sometimes termed "brackish."

Brackish or highly mineralized waters—often locally termed "salty," "gypsum," "gyp," "alkali," "hard," or "very hard"—contain excess salts and minerals or total dissolved solids, chiefly sodium, calcium, magnesium, sulfate, chloride, and bicarbonate. Nitrates, fluorides, and potassium are found in smaller amounts. These waters have been avoided wherever possible as municipal sources. Where no other sources have been conveniently available, highly mineralized waters containing up to 3,000 ppm total dissolved solids (or even more in a few isolated cases) have been used without significant mineral reduction as public supplies. The Saline Water Conversion Task Group of the American Water Works Association reported in 1961[2] that 1,066 municipal water utilities in the United States and Canada had raw water with total dissolved solids of 1,000 to 3,000 ppm and 31 had water in the range of 3,000 to 10,000 ppm. Over 3,000,000[3] people in the United States receive water with a total dissolved solids content in excess of 1,000 ppm.

The mineral content of some important water sources is increasing as use intensifies. For example, the U.S. Department of the Interior recently reported that the Colorado River, serving supplemental water to nearly 10 million people in southern California, would have had an average total dissolved solids content below Hoover Dam of 685 ppm "under historic conditions" in the years 1941–1961. Under the "expected condition, with all authorized projects and projects proposed for authorization in operation," the projected value will be 960 ppm.[4]

Dominy[5] summarized the connection between water usage and water mineralization in a recent address as follows:

> In connection with water pollution control, great emphasis has been placed on the mineralization of water. However, it is not so clearly understood that when water is put to work and beneficially consumed, there is a concentrating effect on any minerals in the water, and the greatest cumulative effect in reduction of water quality usually develops through use and reuse of the same water as it moves progressively downstream. Paradoxically, the greatest economic benefit from a given water supply is usually achieved by this same procedure.

During the past several decades, as water use has increased and the quality of available sources has degraded, both official agencies and the public have focused greater attention on water quality. The U.S. Public Health Service Drinking Water Standards of 1946 and 1956,[6,7] for example, recommended maximum total dissolved solids content of domestic water supplies of 500 ppm but noted that water of up to 1,000 ppm was acceptable if no better supplies were available. The 1962 Drinking Water Standards[8] now recommends 500 ppm maximum total dissolved solids with no mention of a higher level. The recently adopted Quality Goals for Potable Water of the American Water Works Association[9] go purposefully beyond the U.S. Public Health Standards and declare that quality water should contain no more than 200 ppm total dissolved solids. These new standards reflect public demand and add impetus to the need for processes capable of reducing mineral content. For example, a study[56] of 400 United States water supplies by the U.S. Public Health Service in 1961–1966 found that half of the supplies contained more than the AWWA goal of 200 ppm total dissolved solids.

Studies have been undertaken of the hidden costs which the use of highly mineralized water imposes upon the consumer. In Buckeye, Arizona, the cost of excess corrosion, soap usage, and bottled water consumption resulting from the use of a 2,200-ppm water was estimated from a door-to-door survey of users at about $120 per year per household.[10] A survey of service life reduction of plumbing and appliances due to highly mineralized water, generally in the 1,000- to 2,000-ppm range in 38 communities showed an average cost per household of $40 per year.[11]

In summary, water-treatment processes capable of reducing saline and mineral content are needed for two purposes: (1) to make useful some of that 99.4 per cent of all the water on earth which is in the seas and ice caps, plus that portion of the land water (probably about one-quarter to one-half) which has a mineral content of more than 1,000 ppm, and (2) to upgrade the quality of highly mineralized domestic water supplies which now serve millions of people in our communities. Only through the widespread use of processes to remove excess mineral content can the Drinking Water Standards of the U.S. Public Health Service and the Quality Goals for Potable Water of the American Water Works Association be attained for most or all of our population. As R. J. Faust, former executive secretary of the American Water Works Association, has written:[12]

> All public water supplies must be safe, but that quality alone is not enough to meet the needs of today's discerning public. The people want and need a water supply that is clear, tasteless and odorless, soft, nonstaining, colorless, noncorrosive, and, if possible, cool. Fortunately, facilities to achieve these criteria are available now. Yet thousands of public supplies in the country fall far short of providing quality water. Here again, it is the management's duty to inform the people of the inferior characteristics of the local supply and to tell them how they may be corrected and what the costs will be.

SOURCES OF SALINE WATER

Saline waters include (1) undiluted seawater containing about 35,000 ppm total dissolved solids (TDS) and (2) brackish water containing from 1,000 ppm to about 10,000–15,000 ppm TDS and are largely represented by highly mineralized groundwaters and diluted seawater.

Seawater

Seawater is available at sea level and at the sea coast. It is important as a major water resource because of the size and importance of coastal communities which can be served by converted seawater (diluted or undiluted) and because of the inexhaustible quantities available. The availability of water-desalting processes is sharply altering traditional concepts of water resource planning. A coastal community can now consider the ocean as a potential freshwater resource. Such a concept was considered a visionary dream a generation ago.

Brackish Water

Sources of brackish water are less obvious and less well known than those of seawater. Brackish waters are widely distributed over the land area of the North American and other continents. Because of their lower mineral content, brackish or highly mineralized waters are, in most cases, less expensive to treat than seawater. Brackish water is found underground[13] as well as in estuaries, rivers, lakes, and certain wastewaters. These sources of brackish water are discussed in more detail below.

Groundwater. The most widely available and, in many ways, the most desirable source of brackish water is brackish groundwater. Brackish groundwater reserves are found in many parts of the world, including the United States, Canada, Mexico, Southern and Western Europe, North Africa, the Middle East, Australia, Western Africa, and South America. Well over half the land area of the continental United States is underlaid by saline waters having total dissolved solids content in the 1,000- to 3,000-ppm range (Fig. 1). Two full-color maps are available from the U.S. Geological Survey,[13] showing the chemical quality of, extent of, and depth to these saline aquifers. Important highly mineralized groundwater supplies occur in arid or semiarid states where freshwater supplies are already at a premium, including Texas, Oklahoma, Kansas, Nebraska, North and South Dakota, parts of Arizona, New Mexico, Colorado, Utah, Wyoming, Montana, Nevada, and California.

In common with most underground waters, saline groundwaters have many desirable characteristics as raw water sources. Groundwater from deep wells is generally low in organic content and therefore may be low in color, taste, and odor; is stable in quality; is normally protected from natural and man-made pollution; is relatively unaffected by intermediate-term fluctuations in rainfall; and is often available close to the point of use. Storage costs are minimized since the aquifer supplies much of the needed storage. Groundwater use for water supply has been impeded in some areas by high mineral content. Now such impurities can be dealt with by the water supply engineer, just as such conventional impurities as turbidity and hardness have been dealt with in the past.

Estuaries. Estuaries of some major rivers extend inland for many miles

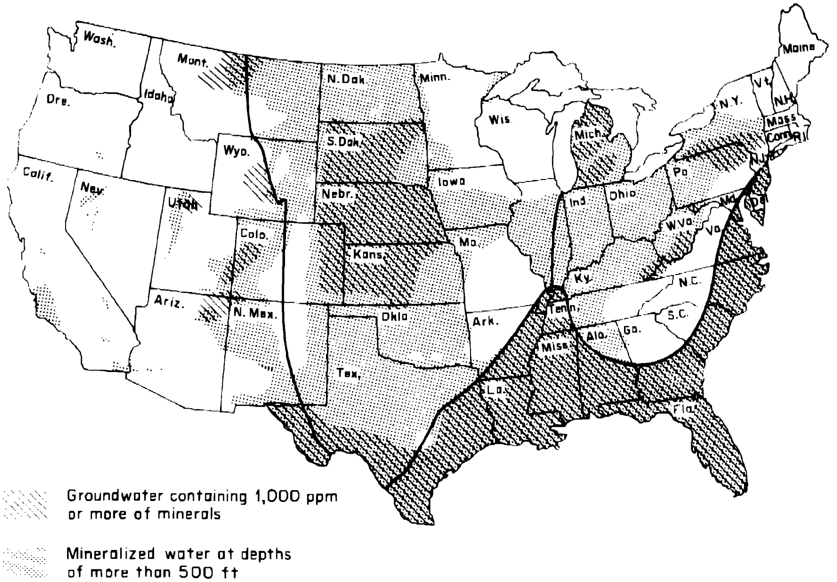

Fig. 1 Preliminary map of the conterminous United States showing depth to and quality of shallowest groundwater containing more than 1,000 ppm dissolved solids[13] (*Ground Water*

and represent major sources of brackish water.[14] Practical salt-removal processes give water engineers a new degree of freedom in dealing with estuarial water problems. In the past, salt had to be avoided at all costs. When, in an emergency, salt appeared, one either had to "live with it," shut down, or move upstream. In designing new facilities, one had to go far enough upstream to avoid salt under the worst rainfall or stream flow conditions one could envision with the records and methods then available. Now, salt can be considered as a pollutant which can be removed at predicted cost. Water sources can now be considered for development further downstream in estuaries that may be closer to existing distribution systems when treatment facilities include salt removal. The cost and feasibility of such downstream sources can be compared directly with the cost and feasibility of sources located further upstream, or with the construction of additional freshwater upstream storage for low flow augmentation.

Many major metropolitan centers in the East, including New York City, have ample freshwater storage facilities during years with average to high rainfalls to handle present and near-future needs. Supplementary water sources will be needed only in drought periods and especially during extended dry periods of 3 years and longer. The Northeast Desalting Report on the New York City situation[14] concluded that over the next 30 years, supplementary water would probably be needed only 20 per cent of the time. The waters of the Hudson River at Indian Point (35 miles north from Times Square), for example, even during drought periods, would be fresh enough to permit 50 per cent of the supplemental water to receive conventional treatment with the other half receiving desalting. This arrangement would minimize operating and maintenance costs. The low capital cost of brackish water conversion processes is advantageous for this service.[15]

Saline Rivers and Lakes. A few major rivers and large lakes are saline or brackish in nature. Some examples in the United States are the Arkansas, Red, Pecos, and parts of the Colorado River, as well as Lake Texoma on the Red River. Attempts are being made to reduce the salinity of some of these streams by control of natural salt pollution sources.[16] These rivers have large flows of water and could benefit major areas surrounding them. The Arkansas River, for example, runs through or near such cities as Wichita, Kansas; Tulsa, Oklahoma; and Little Rock, Arkansas. It is now possible to compare the cost of the proposed natural pollution control measures with the cost of removing the salt at points of local withdrawals for municipal or other beneficial uses.

Wastewaters. Three of the major beneficial uses of water result in substantial increases in its mineral content—namely irrigation, industrial cooling by evaporation, and municipal use.[5] In many parts of the Southwest, the drainage water from irrigation projects will have on the order of double to triple the mineral content of the raw water initially applied. For example, the New and Alamo Rivers in California which are formed by drainage from irrigation projects in the Imperial Valley using Colorado River water have total dissolved solids content in the neighborhood of 2,000 to 3,000 ppm, whereas the raw water from the Colorado River has 600 to 900 ppm total dissolved solids.

The wastewater from municipal sources will usually show an increase of 300 to 400 ppm in total dissolved solids content above that of the public water supply of the community. Thus, the total dissolved solids in the sewage effluents from such cities as Los Angeles and San Diego reflects both the relatively high total dissolved solids content (300 to 900 ppm) of their "fresh" water sources and the 300- to 400-ppm increment from municipal use.

PRACTICAL APPLICATIONS

Status of Saline Water Conversion in Water Utility Practice

The following summary of saline water conversion plants currently in water utility operation and of projects being studied for future use on a larger scale will illustrate the degree of practical usefulness which has been attained by saline water conversion processes.

Various forms of distillation—notably multistage flash (MSF), long-tube vertical (LTV), and vapor compression (VC)—are the principal processes in use on seawater. Electrodialysis (ED) is the principal process in use on brackish or less highly mineralized water. Freezing, reverse osmosis (RO), and ion exchange (IE) are in the development and pilot plant stage. A brief summary of the principles, characteristics, and status of each of these processes is contained in the section on "Saline Water Conversion Processes," pages 612–622, along with references to more detailed data in the literature.

Water Utility Plants in Operation

There are in operation or under construction in the United States seven saline water conversion plants owned and operated by water utilities with an aggregate capacity of approximately 5 mgd (see Table 18-1). Five of these treat brackish water of 1,000 to 3,000 ppm total dissolved solids by the electrodialysis process, and two treat seawater by the multistage flash distillation process. In addition to these seven plants, Table 18-2 lists eight *demonstration* plants in the United States with an aggregate capacity of approximately 7 mgd. These demonstration plants are operated primarily to obtain technical and economic data and experience, although they do furnish some product water to water utilities, generally without charge or at prices which are significantly less than the cost of production. Five of these plants are funded and operated by the Office of Saline Water of the Department of the Interior.

The use of saline water conversion plants for water utility purposes has been more widespread and on a larger scale abroad than in the United States, and particularly in developing countries. Table 18-3 lists 20 plants or complexes of plants in operation or under construction outside the continental United States, each of which exceeds 1 mgd in capacity. The aggregate capacity of these plants is about 67 mgd. All use some form of distillation and most of them use MSF distillation. The largest capacity aggregate is in Kuwait with about 20 mgd (and more planned). The two Netherlands Antilles of Aruba and Curacao have about 10 mgd combined, Mexico and the Netherlands each about 7 mgd, and the Canary Islands 5 mgd.

The Office of Saline Water has reported[17] that as of January 1, 1968, there were 627 plants of more than 25,000-gpd capacity in operation or under construction with an aggregate capacity of 220 mgd. Plants over 300,000-gpd capacity represented 17 per cent of the total number of plants and 79 per cent of the total capacity. Included in the above totals are 45 plants with an aggregate capacity of 58 mgd which started construction in 1967. It is estimated that approximately 10 per cent of the number of plants and 60 per cent of worldwide capacity listed by OSW is for water utility purposes. The balance is for boiler, oil refinery, military, hotel,

TABLE 18-1 Saline Water Conversion Plants Owned by Water Utilities in the U.S.A. (as of July 1, 1969)

Location	Owner	Capacity, gpd	Process	Start-up date	Raw water TDS, ppm
Coalinga, Calif.	City of Coalinga	28,000	ED	1959	2,400
Buckeye, Ariz.	Town of Buckeye	650,000	ED	1962	2,200
Port Mansfield, Tex.	Port Mansfield PUD	250,000	ED	1965	2,400
Catalina Island, Calif.	Southern California Edison	150,000	MSF	1965	35,000
Key West, Fla.	Florida Keys Aqueduct Commission	2,600,000	MSF	1967	35,000
Dell City, Tex.	City of Dell City	70,000*	ED	1967	2,700
Siesta Key, Fla.	Siesta Key Utilities Authority	1,200,000†	ED	1969	1,300
		4,948,000			

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*Expanded from 50,000 to 70,000 gpd in 1968.

†Expandable to 2 mgd.

Table 18-2 Saline Water Conversion Demonstration and Test Bed Plants Furnishing Utility Water in U.S.A. (as of July 1, 1969)

Location	Owner	Water purchaser	Capacity, gpd	Process	Start-up date	Raw Water TDS, ppm
Freeport, Tex.	OSW	City of Freeport	1,000,000	LTV	1961	35,000
(San Diego, Calif. #1) ...	(OSW)	(City of San Diego)	(1,000,000)	(MSF)	(1962*)	(35,000)
Webster, S. Dak.	OSW	City of Webster	250,000	ED	1962	1,500
Roswell, N. Mex.	OSW	City of Roswell	1,000,000	VC	1964	15,400
Coalinga, Calif.	UCLA	City of Coalinga	8,000	RO†	1965	2,500
San Diego, Calif. #2	OSW	City of San Diego	1,000,000	MSF	1967	35,000
San Diego, Calif.	OSW	City of San Diego	2,500,000	MSF	1968	35,000
Plains, Tex.	Vendor	City of Plains	100,000	RO‡	1969	2,000
Bessie, Okla.	Vendor	Town of Bessie	10,000	RO§	1969	3,000

*Moved to Guantanamo in 1963.

†Tubular-type reverse osmosis.

‡Hollow-fiber-type reverse osmosis.

§Spiral-type reverse osmosis.

or other industrial or special use. Of the world total, 36 plants with approximately 5-mgd aggregate capacity utilize ED. Two pilot or demonstration plants with 0.1-mgd total capacity use RO, and four with 0.6 mgd use freezing.

From the above data, a number of conclusions can be drawn:

1. Saline water conversion has to date found more practical water utility use outside of the United States than within it, and in developing countries rather than in more developed countries.

2. In both number of installations and size of such installations, seawater distillation has been the most frequently used process. Electrodialysis has been the method of choice for brackish water desalting.

3. In the United States, brackish water treatment has predominated in cases where the installation was made on an economic rather than a demonstration basis. However, experimental, developmental, and demonstration seawater units of substantial size are in operation and in prospect in the United States.

In the early stages of development, and particularly in small sizes, the cost of saline water conversion has been relatively high. These circum-

TABLE 18–3 Saline Water Conversion Plants or Complexes of More Than 1 mgd Capacity Outside of Continental U.S.A.

Location	Number of units	Total capacity	Process*	Feedwater
Aruba	5	2,688,000	ST	Seawater
Bahamas (New Prov.)	2	1,440,000	MSF	Seawater
Canary Islands	4	5,284,000	MSF	Seawater
Ceuta (Sp. Morocco)	2	1,055,000	MSF	Seawater
Cuba (Guantanamo)	3	2,250,000	MSF	Seawater
Curacao	5	6,098,000	ST/MSF	Seawater
Israel (Eilat)	1	1,000,000	MSF	Seawater
Italy (Taranto)	2	1,200,000	MSF	Seawater
Kuwait (Shuwaikh)	20	2,400,000	ST	Seawater
(Shuwaikh)	10	12,000,000	MSF	Seawater
(Shuaiba)	4	6,000,000	MSF	Seawater
Malta (Valetta)	1	1,200,000	MSF	Seawater
Mexico (Rosarita)	2	7,500,000	MSF	Seawater
Netherlands (Terneuzen)	2	7,650,000	MSF	Seawater
Qatar (Doha)	2	1,800,000	MSF	Seawater
USSR (Kazakh)		1,300,000	LTV	Seawater
Virgin Islands (St. Thomas)	1	1,000,000	MSF	Seawater
(St. Thomas)		2,500,000	MSF	Seawater
(St. Croix)	1	1,500,000	MSF	Seawater
Venezuela (Pt. Cordon)	1	1,440,000	MSF	Seawater

* For explanation of process initials, see "Status of Saline Water Conversion in Water Utility Practice," pp. 592–593. "ST" is multieffect, straight-tube — a now-obsolete type of evaporator.

stances historically limited the early applications of saline water conversion to situations where water was high in value, e.g., military, shipboard, or island use; use in isolated locations, particularly for small supplies[18]; use in well-financed industries such as oil and mining exploration or resorts; applications where the value of the water itself was high, such as in the bottling of carbonated beverages, and in the preparation of boiler feedwater for high-pressure boiler plants.

The water utility industry in the United States, however, is interested in saline water conversion primarily to the extent that it will be able to compete with alternate sources of conventionally supplied water.[19] Five out of the seven operating water utility installations in the continental United States using saline water conversion utilize brackish water as a source because the treatment of brackish waters is considerably less expensive at any given scale of production than the alternate treatment of seawater, except under the most unusual circumstances.

The reductions in cost of saline water conversion for both seawater and brackish water have been so great in the past decade that saline water conversion processes are now beginning to merit serious consideration as alternatives for large-scale water supply in the United States. The case histories of the selection of three of the seven water utility plants in commercial operation in the United States illustrate some of the practical principles involved in the selection and use of saline water conversion plants.

Buckeye, Arizona. In Buckeye,[10] abundant highly mineralized well water containing approximately 2,000 ppm of dissolved solids had been supplied prior to 1961 by an existing municipal system to over 600 water customers who paid an average of about $5 per month for the untreated water. In 1961, a survey taken by the Buckeye Chamber of Commerce revealed that the highly mineralized water caused the average customer to spend an additional $10 per month for purchase of bottled water, effects of hardness, and excess corrosion. The differences between the 2,000-ppm water and an ED-treated water of 500 ppm were demonstrated to the community. By a margin of approximately 2:1, the citizens voted to raise the water rates by about $7.50 per month per customer, to treat all of the city's municipal water by ED. The Buckeye desalting plant, of 650,000-gpd capacity, went on-stream in 1962. The construction cost of $305,000 was financed through the sale of water revenue bonds by competitive bidding through normal underwriting channels. The Buckeye case demonstrates the willingness of water consumers to pay more for good water when given a choice.

Key West, Florida. The city of Key West, Florida, is on an island connected to the mainland by a causeway. A 130-mile, 18-inch aqueduct was built in 1944 to serve the city and the Naval base with good-quality well water from wells in southern Florida. About 1962, it appeared that the capacity of this pipeline was becoming insufficient due to growth of population in the Keys. Additional booster pump stations were added to the pipeline, bringing its capacity to about 5 mgd. Studies of alternative water supplies, including the building of an additional aqueduct and seawater desalting plants of various sizes and energy sources indicated that the cost of distilling seawater would be considerably less than the cost of developing a new aqueduct. Design was undertaken of a multistage flash distillation plant with construction beginning in 1966, and production in 1967. With total capital cost of about $4,300,000, the plant has a capacity of 2.6 mgd. The total cost of converted water is estimated at about 85 cents per thousand gallons at about 90 per cent load factor. Seawater concentration is about 35,000 ppm TDS; finished water composition is less than 50 ppm, but this product is treated with limestone and other stabilizers to reduce corrosion (Fig. 2).

Siesta Key, Florida. The Siesta Key Utilities Authority was formed to provide water and sewer service to an unincorporated area of Sarasota County adjacent to the city of Sarasota. The area had been developed with relatively high income homes served by private wells or small neighborhood utilities with water of high mineral content. Highly mineralized water of approximately 1,300 ppm TDS (including 700 ppm sulfates) was available in quantity in the area. Alternatives included development of a shallow well water supply of marginal mineral content 10 to 15 miles inland, purchase of water of marginal mineral content from one or more nearby utilities, or treatment of the available water supply. In this case, treatment of the available supply appeared to be the best alternative for obtaining reliable, high-quality water. A brackish water desalting system of 1.2-mgd initial capacity with some features sized for 2 mgd started operation in 1969. Capital cost is around $600,000, including building and pretreatment by aeration and filtration to remove hydrogen sulfide and iron. Finished water will contain about 450 ppm dissolved solids and 250

Fig. 2 2,620,000-gpd seawater desalting plant for the Florida Keys Aqueduct Commission, Key West, Florida *(Westinghouse Electric Corporation)*.

Fig. 3 Interior view of the 1.2-mgd (expandable to 2.0 mgd) electrodialysis (ED) desalting plant built for the Siesta Key Utilities Authority, Sarasota County, Florida *(Ionics, Incorporated).*

ppm sulfates. Operating and maintenance costs for the conversion of the local well water are estimated at 18 cents per thousand gallons, and total costs (including capital amortization) at about 33 cents per thousand gallons at a predicted 61 per cent load factor (Fig. 3).

Studies of Possible Future Large-scale Saline Water Conversion Projects

Potential future water supply projects based on desalting, and varying in capacity from a few hundred thousand to as much as 2 or 3 billion gallons per day, have been studied by water supply agencies in the United States and abroad. Important overseas studies in the 100-mgd to 1-bgd capacity range have included proposed plants in Egypt, Israel, Mexico, and Spain. The following summaries from selected reports on future possible desalting projects in the United States will illustrate the variety and scope of the projects considered.

"Potentialities and Possibilities of Desalting for Northern New Jersey and New York City." In 1965, because of the worsening drought, President L. B. Johnson constituted several federal government agencies as a Northeast Desalting Team to investigate the potentialities and possibilities of desalting in the Northeast.

They found[14] that large dual-purpose seawater desalting plants (300 mgd) can be built for the Northeast and would provide increments of safe yield during critically dry periods, but would cost about twice as much as withdrawing freshwater from the Hudson River based on 1965 technology.

The study also found that the lower Hudson River is a large source of brackish water, with salt levels in the estuary much lower than those for seawater. Based on 1965 technology, desalting the brackish estuarial water by ED would cost about 20 per cent less than desalting seawater—but still substantially more than taking freshwater.

> Cost estimates derived in this study are based on current desalting technology and available cost data for baseload designs. Major capital and operating cost reductions from those shown in this report are possible through designs specifically optimized for peaking operation. Further reductions may be anticipated from advancements in desalting technology to be expected by the time the additional supplemental water supplies are required in the Northeast.

In 1968, the State of New York and the U.S. Department of the Interior announced a jointly funded study of the use of large ED plants of 25- to 300-mgd capacity on estuarial waters including those of the Hudson. This study was stimulated by the Northeast Desalting Report and by work on optimization of an ED system on the Hudson River carried out by a private engineering firm[20] which suggested significantly lower figures for a properly optimized system than those cited above.

"Augmentation of the Colorado River by Desalting of Sea Water."[21] This report prepared by the Bureau of Reclamation for Congressional Hearings early in 1968 represents the most ambitious and controversial proposal yet made on seawater desalting. The report states:

> Of the four principal potentials for augmenting Colorado River water supply—desalting of sea water, surface water imports from basins of surplus water supply, weather modification, and water salvage measures—only the first two offer potentials of the magnitude necessary for adequate long-range solutions.
>
> Sooner or later, recourse must be made either to the unlimited seas or to surface water imports if the foreseeable water needs of the Colorado River Basin are to be met.

Cost estimates for freshwater from seawater of slightly under 10 cents per thousand gallons at a southern California seaside site and 25 cents per thousand gallons conveyed 4,000 ft up and several hundred miles inland to Lake Mead were presented in this report. The report projected staged construction of plants aggregating 2.0 bgd in the years 1990 to 2010. The total cost was estimated at $1.4 billion for the nuclear reactor–desalting plants and about $2.7 billion including the conveyance system.

According to press accounts[22] there was sufficient question of the validity of these figures among key members of the House Interior Committee who received this report, so that a requested feasibility study was not authorized at that session.

Chairman Wayne N. Aspinall of the House Interior and Insular Affairs Committee made the following comments on this subject in September, 1968, while recommending approval of Colorado River legislation[23]:

> Top priority is to be given to determining the most economical means of augmenting the water supply of the Colorado River since the Colorado Basin is the most critical watershort area of the Nation. All possible sources of water must be considered, including water conservation and salvage, weather modification, desalination, and importation from areas of surplus. However, studies of any plan for importation of water into the Colorado River Basin from other drainage

> basins lying outside the Colorado River Basin States are prohibited for a period of ten years. During this moratorium all other phases of the westwide water study will go forward and after the moratorium ends the overall westwide study can continue without restriction.

Representative Saylor of Pennsylvania, the ranking Minority member of the same committee, on the same occasion, responded:

> The major premise espoused by the proponents of this legislation as the justification for its controversial provisions is the shortage of water in the Colorado River and the fact that the river has never produced the water expected of it. If this is in fact true, then it would follow that the legislation should not contain provisions which guarantee the availability of 4.4 million acre-feet of water in perpetuity to the State of California. Is there now some guarantee from the Almighty that we shall have available in perpetuity at least 4.4 million acre-feet of water in the river? I think not.

The impact of saline water conversion on a major regional water problem such as that of the Colorado River is illustrated by these quotations. A saline water conversion plant has the potential of supplying a specified amount of water at a specified location, in spite of the uncertainties of rainfall and runoff.

"The Potential Contribution of Desalting to Future Water Supply in Texas." This report,[15] performed by a nonprofit research institute for the Texas Water Development Board and the Office of Saline Water, screened all Texas cities of more than 1,000 population and identified 37 cities where detailed analyses of water supply alternatives appeared worthwhile.

Costs for providing water supplies from desalting versus the costs of providing water supplies from the least expensive conventional sources were compared. Eleven Texas cities were identified in which the unit cost for desalting water was less than or about the same as the unit cost of water from conventional sources. Comparisons included costs for water production, transportation, treatment, processing, and brine disposal. For the eleven cities, the capital costs for the water supplies based on treatment of brackish waters ranged from 20 per cent to 57 per cent of the capital cost for a "conventional" supply.

> In favor of desalting in all eleven cities is the lower initial capital investment required for desalting as compared to development of conventional water supplies. Although unit costs of both may be relatively close due to higher operating and maintenance costs for desalting, the lower initial capital costs should be of great interest to all cities, and especially to those with limited borrowing power.

"The Economics of a Regional Municipal Desalting System in the Lower Rio Grande Valley of Texas."[24] This report by and for the same agencies as above compared ED treatment of brackish waters and distillation of seawater to provide 62 mgd of supplementary 500-ppm TDS water to nine

cities in the lower Rio Grande valley of Texas. Estimated unit delivered water costs varied from $87 per acre-foot for a triple-purpose distillation, power, and ammonia-producing complex costing $87,000,000 to $101 per acre-foot for a single-purpose ED plant costing $28,000,000. These costs include distribution systems costing $8,000,000 for the ED plant and $13,500,000 for the distillation plant.

"Resolution of the Unsuitability for Municipal and Industrial Use of the Water Presently Stored in the Foss Reservoir (Oklahoma)."[25] Intensive use of rivers in arid and semiarid regions leads to an increase in mineral content and an important application for desalting of brackish waters. The first such case to attract national attention is that of the Foss Reservoir on the Washita River in western Oklahoma. In 1956, the Congress authorized Foss Reservoir, and in 1961 the dam forming the reservoir was closed. It was known that Washita River water was relatively high in sulfates and total dissolved solids and it was expected that the water would contain about 750 ppm total dissolved solids and 391 ppm sulfates. A group of cities in Oklahoma to be served by municipal water from this reservoir agreed to repay to the federal government approximately $7.5 million over a 50-year period for a portion of the cost of the reservoir and an aqueduct. The project was completed and payments were begun by the communities. It was then discovered that the impounded water contained about 1,800 ppm total dissolved solids and 900 ppm sulfates. A special consulting board convened by the Secretary of the Interior in 1967 reviewed the project and found that the water in Foss Reservoir was not suitable for municipal use, that long-term natural quality improvement was not to be expected, and that the Foss Reservoir water appears to be the only real solution to the needs of the contracting communities.

Members of the Oklahoma congressional delegation introduced a bill in Congress in 1967 to authorize immediate construction of a 2- to 3-mgd desalting plant to solve this problem. However, the bill was modified to provide for further study of alternatives before the plant construction is authorized.[26]

"Preliminary Feasibility and Economics of Desalting Brackish Waters in Candidate Areas of West Texas." This report,[27] prepared by a private engineering firm for the Texas Water Development Board and the Office of Saline Water, studied the feasibility and economics of developing a supply of freshwater in parts of west Texas by the desalting of available brackish groundwater sources on a scale of 2 to 20 mgd. Processes considered included various forms of distillation, ED, RO, and freezing. This report compared the costs of the desalted water with the costs of alternative, imported supplies to provide additional water for municipal and industrial water supply.

The estimated costs of desalting water ranged from 36 cents per thousand gallons in El Paso County to as high as $1.15 in an area with a much higher salinity water. While the lower costs appeared competitive with imported supplies, there was uncertainty with regard to the quantity and quality of brackish water available to support operation of large-scale desalination plants.

COSTS AND CHARACTERISTICS

General Characteristics

Saline water conversion plants have certain basic characteristics which differ from those of typical conventional water supply projects. As compared to conventional projects, saline water conversion projects may in favorable circumstances

1. Require less capital investment
2. Be less subject to rainfall or safe yield uncertainties
3. Require less land area
4. Minimize right of way, surveying, and geological uncertainties
5. Minimize water rights problems, and hence, political and legal delays
6. Require less time to complete from inception to water production, and hence, minimize the impact of inflation
7. Have a higher component of manufactured equipment and a lower component of construction labor
8. Yield a more predictable and controllable quality of product

The capital cost advantage for saline water projects may be amplified since saline water plant equipment is modular and can be readily expanded to meet increasing demand—keeping load factor or utilization factor high. The typical conventional project is usually built with substantial excess capacity and therefore operates at low utilization factors in the first years of its existence.

The combined direct operating and maintenance costs of saline water conversion projects (both seawater and brackish water) will generally be higher than the combined operating and maintenance costs for conventional projects. On brackish waters of low total solids the direct operating costs for conversion may approximate the direct operating costs for conventional projects requiring considerable pumping and conventional water treatment. However, the maintenance costs of all saline water conversion projects (replacement of membranes, resins, or metal parts of distillation plants) will be significantly greater than those for conventional projects.

With lower capital costs, but higher operation and maintenance (O&M) costs, economic comparisons between conventional and saline water projects will be sensitive to the rate at which capital is charged, the rate at which future O&M costs are discounted, and to the load factor or per cent utilization of the project.

As we reach the end of the 1960 decade, there has been intensifying competition for public funds and a substantial increase in interest rates. The relatively low level of capital charges which have been allocated to water resource projects in the past has come under increasing criticism.[28] Many economists now believe that a return to the relatively low interest rates of past years is unlikely, and that we must live in a world that puts higher charges on public capital invested in water supply projects. There have already been changes in federal regulations to increase such charges. The changes so far made are probably small in relation to those which will face project planners in the 1970s. However one may view the merits of this trend, it now seems certain that generally higher interest and discounting rates will be used both in evaluating alternatives before projects are authorized and for determining the proper level of charges after projects have been built.

This upward shift in cost of capital will be of substantial importance in determining the degree of future water supply investment directed to saline water sources as compared with conventional sources.

Seawater Conversion. Seawater conversion processes provide the extraordinary advantage of opening the seas as an unlimited source of water. This could be a boon to mankind, especially for those people living in freshwater-starved areas. Also, political objections to the taking of seawater for conversion to freshwater are minimized or nonexistent as compared to the taking of freshwater supplies from other areas. For example, additional freshwater for southern California must come from northern regions of the state, adjoining states, or even the neighboring country of Canada.[29] Regardless of the magnitude or current state of use of the freshwater resources of these other regions, there have been and undoubtedly will continue to be political objections to their importation into southern California.[23] No such objections can be anticipated for the taking of any quantity of seawater.

As the distance and cost of development for new "fresh" water supplies increases, the capital cost of seawater conversion equipment can be expected to become less than the capital cost of distant freshwater supply projects.

Present-day seawater conversion plants are much more efficient users of heat energy than formerly, but large plants will still be large users of such energy. Since relatively low-grade (low-temperature) energy is suitable for distillation in modern plants, the integration of seawater distillation equipment with nuclear or fossil-fired steam plants which also produce electrical power can be attractive. These dual-purpose plants are estimated in some situations to lower the cost of freshwater produced.

Removal of excess dissolved salts and minerals from water always requires the disposal of salts and minerals so removed. Disposal of the excess salts and minerals back into the sea is an acceptable and relatively low-cost method of waste disposal, which is convenient for seawater conversion processes.

All saline water processes, and particularly those treating highly saline waters such as seawater, are bound to use energy in relatively large quantity. The technology of energy production has improved markedly over the past 50 years, and most authorities predict that such improvement will continue for the foreseeable future. Thus, the expenditure of energy to produce freshwater should become an increasingly better "economic tradeoff" in future years.

There are some countries or situations where the only conceivable source of freshwater is the sea. Islands are a typical example. The development of the economy of such islands can only proceed if freshwater can be provided by seawater conversion. The first two cities in the United States to use seawater conversion in a public utility supply are Key West and Avalon, both of which are on islands.

Brackish Water Conversion. The cost figures in this chapter for brackish water conversion are for the ED process, on which the most published data and field experience over a period of years are available. Newer processes being developed for brackish water conversion (such as RO or IE) have cost goals which approximate the published data for ED. Hence, ED costs are used throughout this chapter as being typical of costs for brackish water desalting.

Conversion of brackish water is an attractive water supply alternative because low total water costs—20 to 40 cents per thousand gallons—can be realized today in plants of relatively modest size and capital requirement.[30]

1. For high load factor operation and using currently developed ED membrane stacks and technology, costs of 30 to 40 cents per thousand gallons or less can be realized for reducing typical brackish waters of 3,000 ppm total dissolved solids and below to 500 ppm on a scale of 2 to 10 mgd. Corresponding costs are 20 to 30 cents on a scale of 10 to 50 mgd.

2. Brackish water conversion plants have low capital investment (compared to distillation or to some conventional water supply methods involving long-distance transmission and/or major impoundment). They are, therefore, attractive for standby, peaking, or low load factor use and for use in areas where capital is limited or expensive.

3. Electrical energy consumption for brackish water conversion is low, varying from 5 to 15 kwhr per thousand gallons for waters of 1,000 to 3,000 ppm. A 10-mgd ED plant on 1,000 to 3,000 ppm water uses 2 to 6 megawatts, at 100 mgd—20 to 60 megawatts.

4. Brackish water conversion processes use electrical energy rather than

heat as their prime utility requirement, thus allowing maximum flexibility of water plant location with respect to energy source location.

5. Membrane process plants have built-in ability to profit from continuing technological improvements. The major replaceable components of such plants—namely, membranes and supports or spacers—through research should continue to improve in effectiveness and thus provide improving efficiency and/or lowering "second-round" maintenance charges for the plant owner during the life of the plant.

General Cost Curves—Brackish Water

Brackish water conversion costs are affected by many variables, including (1) type of process chosen, (2) size of plant, (3) chemical composition and temperature of water to be treated, (4) degree of mineral removal required, (5) unit cost of electrical energy, (6) climate and other construction conditions, (7) the annual load factor, (8) the amortization or interest rate, (9) life of components such as membranes, resins, or tubes, (10) degree of pretreatment required, and (11) labor and maintenance costs.

Generalized costs for relatively favorable conditions were cited in the secton "Brackish Water Conversion," page 605, and are shown in convenient graphical relationship in Figs. 4 and 5. These costs are for the ED process, 90 per cent load factor, warm waters and moderate to warm climates, reduction of mineral content to 500 ppm total dissolved solids, electrical energy rates from 4 to 8 mils per kwh, and 7 per cent amortization charge based on capital investment.[30]

Figure 4 shows the required capital investment in an ED plant in dollars per gpd (gallons per day) for capacities of 500,000 to 100,000,000 gpd and for nominal total solids contents of 900 to 3,000 ppm, as of 1968.

Figure 5 shows the total cost of water produced by ED facilities in the same range of capacity and solids content. The costs include operating, maintenance, and amortization costs for the conversion from saline to fresh.

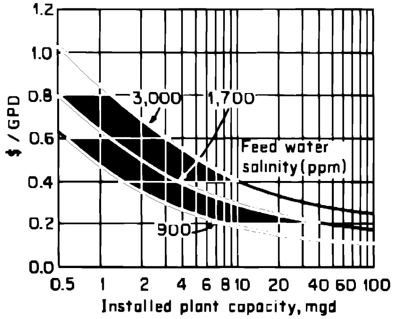

Fig. 4 Total investment cost in dollars per gpd (ED brackish water plants).

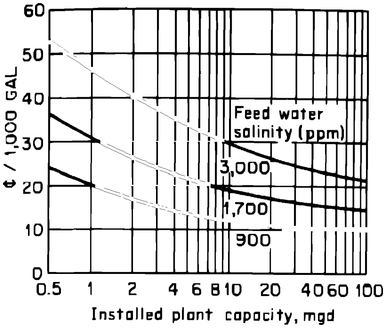

Fig. 5 Total water cost in cents per thousand gallons (ED brackish water plants).

The costs in Figs. 4 and 5 do not include the costs of collecting the brackish water, storing or distributing the treated product, or disposing of the brine.

General Cost Curves—Seawater

Seawater conversion costs are affected by many variables including: (1) size of plant, (2) chemical composition of water to be treated, (3) degree of purity required in the product, (4) unit cost of electrical energy and thermal energy, (5) climate and other construction conditions, (6) ambient and water temperature, (7) annual load factor, (8) amortization or interest rate, (9) estimated life of the components, including heat transfer area, and (10) type of cycle chosen.

Figure 6 shows the total capital cost for multistage flash distillation plants versus capacity, not including steam generation equipment, for plants of 1- to 50-mgd capacity. These costs vary from about $1.5 million to approximately $35 million. The steam generating plant costs add approximately another 20 per cent to these figures.[31]

Principal operating and maintenance costs include electrical power, fuel, chemicals, supplies and maintenance material, operating and maintenance labor, plus payroll extras and overhead. Most plants in the 1- to 5-mgd range now have total estimated operating costs, under relatively favorable conditions (Gulf Coast or southern California), in the neighborhood of 75 cents to $1 per thousand gallons at load factors in the neighborhood of 90 per cent. In the 10-mgd range, some estimates have been made as low as 40 cents per thousand gallons, including all costs; but these are still subject to confirmation by actual experience, particularly with respect to the cost of maintenance due to corrosion and replacement of heat transfer area.

At load factors below 90 per cent, the cost of water produced from seawater plants increases relatively rapidly, since unit capital costs per gpd of capacity are generally several times higher for seawater conversion plants than for brackish water plants.

Effect of Load Factor on Costs

Annual load factor is the ratio of the actual yearly output of water from a plant to the capability of that plant on a year-around, 24-hour basis. Most governmental studies of desalting economics to date have been based on load factors of 90 per cent or greater. This practice results in the lowest reported unit costs—but is not applicable to many situations. Water supply facilities rarely operate at such high load factors because of (1) seasonal fluctuations in amount of water used, (2) provision of excess capacity as a safety factor, and (3) allowance for future growth. For water supply facilities serving the entire water supply of a municipality in the United States, annual load factors in the 50 to 70 per cent range are common. The brief table below shows the effect of load factors of 50, 70, and 90 per cent on the total water costs for 3-mgd ED facilities treating 1,700-ppm water, according to the data of Figs. 4 and 5.

Load factor, %	*Total water costs—1,700-ppm feed*
90	24¢/1000 gal
70	27¢/1000 gal
50	32¢/1000 gal

Dual-purpose Plants

Power and Water Pricing. Much attention has been given to the integration of fossil-fuel, or nuclear-fired steam plants with electric generating

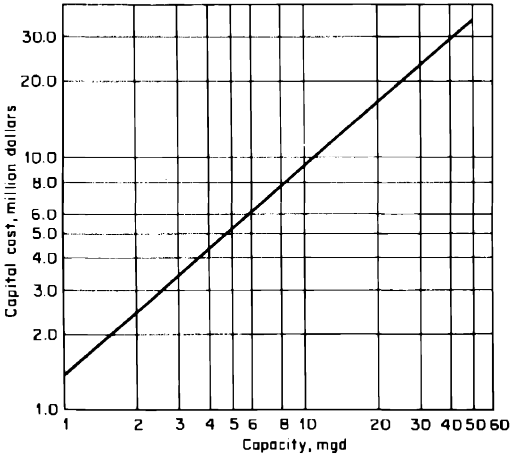

Fig. 6 Multistage flash-distillation plant costs: total capital cost versus capacity, not including steam generating equipment *(U.S. Department of the Interior, Office of Saline Water).*

plants and seawater distillation plants. Such dual-purpose plants reduce fuel costs for distillation by double use of steam and by crediting economies realized from large-scale operation to water costs. Dual-purpose projects also make it possible to subsidize the production cost of water with part of the sales revenues from power without calling on any outside source of income. However, the cost advantage of dual-purpose seawater distillation and power generation projects is usually purchased at the sacrifice of some flexibility in both the siting and operation of the facilities involved, and requires the commitment of much more capital.

Brackish water plants can also be designed and built in conjunction with new electric generation capacity to realize dual-purpose projects. One can plan a large new power facility, add in the load for the desalting plant as an incremental capacity increase, credit most or all of the benefits of the low incremental cost of power so generated to the plant, and operate the facility to take maximum advantage of the interruptibility and peak-shaving characteristics of the plant load. Dual-purpose brackish water desalting and power generation projects have the same social and political "rate-setting" advantage as other types of dual-purpose power and water projects—but will generally have greater flexibility of siting and operation and require less capital.

Waste Heat Utilization. In cases where ED or RO plants are built at or near power generating stations or other sources of low-grade waste heat (100 °F or so), this thermal energy can be used to increase the efficiency of desalting since the efficiency of membrane processes increases at higher temperatures. Generally, ED desalting efficiency rises 1 per cent per degree Fahrenheit in the range of 40° to over 100 °F. With current components, a feedwater temperature of 100 °F is optimum. With components under development, optimum temperatures for ED desalting will rise to at least 120 °F and may, in time, go as high as 180 °F. At 140° to 180 °F, ED desalting of seawater may become competitive with distillation. For RO, the effect of temperature is less well explored, but is probably similar to that for ED.

WASTE DISPOSAL

Nature of Waste

Saline water conversion plants remove salts and minerals from saline waters, producing desalted water of lower mineral content and concentrating the removed salts in a waste stream of higher concentration. Virtually no salts or minerals are added by the saline water conversion processes now in use. The only salts or minerals which appear in the waste streams from most saline water conversion plants are those initially present in the raw water. In most cases, the waste streams from saline water conversion plants, particularly those using inland brackish groundwaters, will be virtually free of COD, BOD, turbidity, color, odor, or any of the objectionable organic materials usually identified in the public mind with the concept of pollution. However, the dissolved mineral content of these waste streams presents an important problem of the saline water conversion field.

From brackish waters in the 1,000- to 3,000-ppm TDS range, the waste stream from a saline water conversion plant will usually constitute from 10 to 30 per cent of the water fed and will contain from 5,000 to 10,000 ppm TDS. This waste stream is sometimes referred to as "brine," but this terminology is misleading since brines usually contain from 35,000 to 250,000 ppm.

From seawater conversion plants, the waste stream will usually contain water ranging from a little above seawater concentration (35,000 ppm) to as much as 70,000 ppm, depending upon the water yield and degree of concentration achieved in the seawater conversion process utilized. Since restrictions on the availability of seawater are usually not a problem at the site of seawater conversion plants, most seawater conversion processes have been designed to waste from 1 to 20 times as much water as is being produced.

Disposal Options and Cost

The method chosen for disposal of saline water conversion plant wastes will depend to a great extent upon the size and location of the plant, the source, salinity, and previous location of the saline water, plus the geology and meteorology of the area. The major options for disposal of saline water conversion plant wastes are as follows:

The Ocean. If the ocean or an outfall reaching the ocean is near the plant, the cost of waste disposal is the cost of conveyance to the ocean. The nature of the waste for most saline water conversion plants is such that disposal into the ocean is likely to cause no significant objection. A possible exception is the temperature and salinity rise associated with the waste stream from a very large (20 to 50 mgd or more) seawater distillation plant.

Inland Saline Lakes, Sinkholes, Dead Seas, e.g., the Great Salt Lake. If the proposed plant is at or near an existing closed drainage depression, whether or not containing water, it seems likely that the disposal of saline water conversion plant wastes to this area would cause no objection, assuming that natural processes will have previously saturated the body of water or area with large concentrations of salts and minerals. The additions from the saline water conversion plant are likely to be small compared to the amounts deposited by natural processes.

Underground. There are a number of well-defined underground formations in certain areas of the country which contain water of very high salinity (e.g., 10,000 ppm total dissolved solids or more). In many cases, carefully controlled disposal of the saline water conversion wastes by injection into these deep aquifers would be considered acceptable, particularly when the wastewater is less saline than that in the aquifer. When brackish waters of 1,000 to 3,000 ppm are being treated and the wastewater is in the 5,000- to 10,000-ppm range, underground disposal of this type may be attractive in areas of suitable geology.

Holding Ponds, Lakes, or Reservoirs. This method—preferably in conjunction with impervious liners or watertight bottoms—has been commonly used in high-evaporation areas such as the southwest part of the United States for disposal of oil field brines. Such ponds are being subject to more stringent regulation as time goes on to protect nearby freshwater supplies. Congress has authorized study of some very large brine reservoirs in the Arkansas-White-Red area to impound existing salt flows. Creation of brine ponds or reservoirs can be an attractive method of disposal in areas of high evaporation rate such as the Southwest. In the case of relatively dilute wastes from inland brackish water plants, consideration is being given to use of the wastewater to create or enlarge recreational or ornamental lakes.

Return to Source or Previous Discharge Area. The simplest method of disposal of the wastes from saline water conversion plants is to return the waste to the source of saline water or to the area where the saline water was previously discharged. This method has been used for a number of existing inland plants of relatively small size. It is an attractive method when one or more of the following criteria are met:

1. An existing flow of saline water is tapped (for example, a saline river).
2. The demineralized, treated water of lower mineral content can also be returned to the same area as the waste.
3. The saline source is of relatively low salinity to begin with, e.g., 1,000 to 3,000 ppm.
4. The saline water was previously used untreated and discharged to the same area untreated.
5. The proposed plant is small.

Disposal to the ocean, to saline lakes, or to the original source or discharge area are methods of ED waste disposal which are low to negligible in cost. However, use of these methods is limited by geographical and regulatory considerations.

Deep well injection or disposal in lined evaporation ponds or reservoirs are more expensive methods, but these methods can be used in a wider variety of situations. Prehn and Sigafoos,[15] using the cost-estimating methods of Holloway and Weaver,[32] reported on saline conversion waste disposal costs for eleven Texas cities in which treatment of a brackish water source appears competitive with alternate conventional supply methods.

These costs added from 1.7 to 3.5 cents per thousand gallons to the desalting cost for nine of the eleven cities, negligible cost in one city, and 9.7 cents per thousand gallons in one (small) city. The city with negligible cost was able to discharge the waste directly to an arm of the ocean. In the other ten cases, use of lined evaporation pits was the method chosen —and was generally half or less than half the cost of deep well injection.

Upgrading of Existing Supply—A Special Disposal Case

In over a thousand communities in the United States and Canada, saline water of 1,000 to 3,000 ppm total dissolved solids is being used for municipal purposes. The sewage effluents from these communities carry excess salts and minerals underground or downstream. If such communities upgrade their municipal supplies by brackish water treatment, their sewage effluents will carry only a fraction of the salt formerly discharged. Mixing of the saline conversion waste with the sewage effluent—or discharging it to the same receiving body which absorbs the sewage effluent neither upgrades nor degrades the salt balance of the area as compared with the situation before treatment was instituted. However, treatment of such municipal supplies makes it more comfortable and more economic for communities to exist.

If the saline plant waste is impounded, injected into the ground, or otherwise disposed of in conjunction with the saline water conversion plant project, then the project can be credited with the dual benefits of (1) making life more comfortable and economic for the community served by the saline water conversion plant and (2) improving the salt balance of the downstream area as well.

SALINE WATER CONVERSION PROCESSES

Distillation

Distillation or evaporation of saline water to produce freshwater goes back to antiquity and is the only process which was seriously used or considered prior to World War II. A few relatively large distillation plants were built for freshwater supply outside the United States before World War II. The necessity of fighting an island war in the Pacific gave impetus to progress in distillation during that war. The development of oil resources in the Middle East after the war gave a further stimulus to distillation development by combining a need for freshwater with an almost unlimited source of low-cost fuel.

Today, distillation is the most widely used saline water process, and is the most highly developed and economical process for use on seawater.

In distillation or evaporation processes, pure water vapor is created by heating saline water. The vapor is separated from the saline water and is condensed to form pure water. If a pound of water is heated and condensed only once (single-effect evaporation), the required heat input is one pound of steam per pound of water or about 1,000 Btu.

The condensation of water vapor to form liquid water produces heat which can be used again and again to evaporate more water at lower and lower pressures, if one supplies additional heat transfer area—at added capital cost. Each reuse (or "effect") of the heat of condensation produces about one more pound of water per 1,000 Btu or per pound of steam. A large number of "effects" are possible, and some modern distillation plants are being built with heat economy factors of 10 or more to 1, i.e., with thermal energy inputs of 100 Btu or less per pound of water produced (800,000 Btu or less per thousand gallons produced). In almost all current designs, the heat required in distillation is supplied by steam, hot gases, or condensing vapor and is transferred through metal tubes to the water being heated or to the water used for cooling and condensing.

There are three principal types of distillation processes currently being used on new construction. These are:

1. Long-tube vertical (LTV) (Fig. 7)
2. Multistage flash (MSF) (Fig. 8)
3. Vapor compression (VC) (Fig. 9)

In LTV distillation, the water to be vaporized flows by gravity down the inside of a long vertical tube, while steam or hot vapor supplies heat on the outside.[33]

In MSF distillation, the water is heated under pressure in tubes and then allowed to expand suddenly or "flash" into a chamber. As some of the water evaporates or flashes, the remaining water cools slightly and then flows into another chamber at lower pressure where it flashes again. The flashed vapor condenses on the outside of tubes in each chamber through

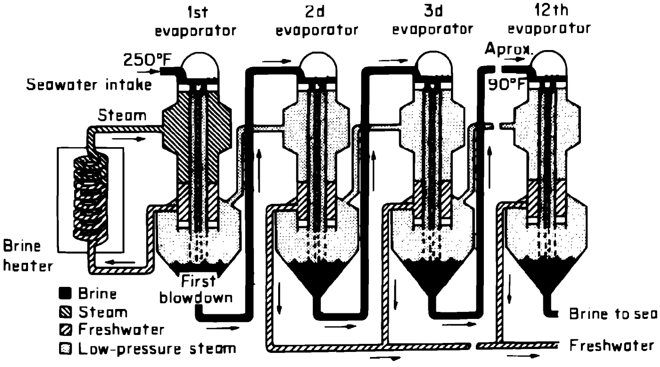

Fig. 7 Simplified diagram of long-tube vertical distillation process *(U.S. Department of the Interior, Office of Saline Water).*

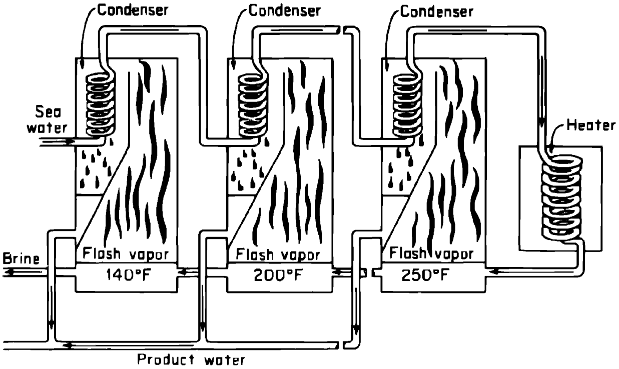

Fig. 8 Simplified diagram of multistage flash distillation process *(U.S. Department of the Interior, Office of Saline Water).*

which cooler water is flowing and picking up heat. The condensed pure water then drips into collecting pans and is pumped to service.[34] Pure distilled water is low in pH and quite aggressive to metals and concrete. Prior to distribution for utility purposes, the pure distilled water is usually further treated by the addition of small amounts of alkali, stabilizing agents such as limestone, or admixture with small amounts of brackish water to provide a more stable product.

In VC distillation, pure water vapor which has been evaporated at a tube surface or in a flash chamber is mechanically compressed (usually by a centrifugal or axial flow gas compressor) to raise its temperature and pressure for use in vaporizing more water. VC cycles must utilize mechanical or electrical energy or work rather than heat as the primary energy input for distillation.[35]

These distillation processes can be combined and there are many indi-

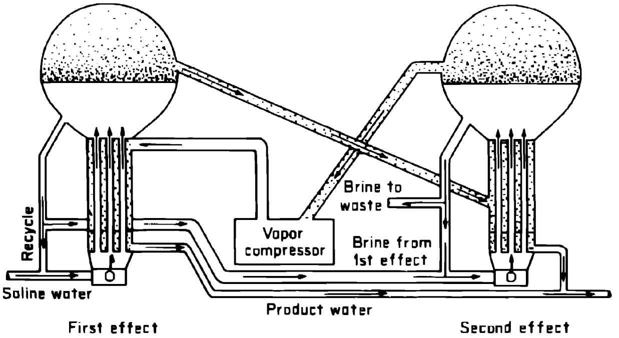

Fig. 9 Simplified diagram of vapor-compression distillation process *(U.S. Department of the Interior, Office of Saline Water).*

vidual modifications, depending upon the amount, type, and cost of available steam, power, water, and other basic factors.[27]

Almost all modern distillation plants are made of metal. Where seawater must be handled, nickel-copper alloys are usually used, and several plants have been built with titanium tubes. For waters of lower salinity, less expensive alloys can be used.

The design of distillation equipment for saline water conversion is a task for the specialist. There is a substantial amount of literature on all phases of distillation: research, development, and operation.[36,37,38] From the point of view of the water utility engineer, the following factors are important:

1. Distillation plants having capacities up to several million gallons per day are in operation at a number of locations throughout the world and have proven their reliability to produce freshwater for utility use.
2. Distillation plants require substantial amounts of thermal energy or electrical power. Accordingly, the cost and availability of energy are important factors in both the design and economic feasibility of distillation plants.
3. Most modern distillation plants, particularly of the MSF type, require large volumes of seawater relative to the amount of water being produced, but this does not usually pose a problem at seaside locations.
4. Long-term data on the life of key components of distillation plants—tubing, pumps, piping, shells, valves—under differing conditions, are needed to allow reliable projection of maintenance costs. These data are available from existing plants.[38]
5. Close attention to water chemistry is essential to maintain the vital heat transfer surfaces of distillation equipment at peak efficiency. The chemistry and biochemistry of seawater vary substantially at different locations and expert advice should be sought on the optimum chemical and mechanical treatments and operating conditions to avoid excessive corrosion, hard scale formation, or marine fouling.

Electrodialysis

Electrodialysis (ED) was developed subsequent to World War II and was the first process to demonstrate that there was a practical method, other than distillation, to desalt water. The principles underlying ED were discussed in the literature for several decades prior to World War II, but practical realization of the process awaited the development of durable ion-exchange membranes in the late 1940s.[39] Today ED is the most widely used process for the treatment of brackish or highly mineralized waters and particularly for those containing between 1,000 and 5,000 ppm total dissolved solids.

In ED, salts and minerals are removed from a stream of saline water through special plastic membranes by the action of a direct electrical current (dc). The salts and minerals pass through the membranes in the form of positively and negatively charged ions. The water from which these ions have been removed flows between the membranes and is collected as a partially demineralized product via manifolds cut through the membranes. The salts and minerals removed from the product stream pass through the membranes into another stream of water which continuously washes the other side of each membrane and emerges through manifolds as a more concentrated waste stream. The amount of electrical current and membrane surface required to desalt a given quantity of water by ED depends upon the amount and type of mineral to be removed. Hence, the cost of ED treatment is also dependent upon the amount and type of mineral to be removed (Fig. 10).

ED plants require pumps to force both product and wastewater between the membranes, a source of dc electricity (usually a silicon rectifier), and an array of membranes called "membrane stacks." These stacks consist of "cation" membranes, which pass positive but not negative ions, alternating with "anion" membranes, which pass negative but not positive ions. Each pair of membranes is separated by a plastic gasket or spacer—generally on the order of 1 mm thick—which contains the liquid between the membranes, directs the flow of liquid past the surface of the membranes,

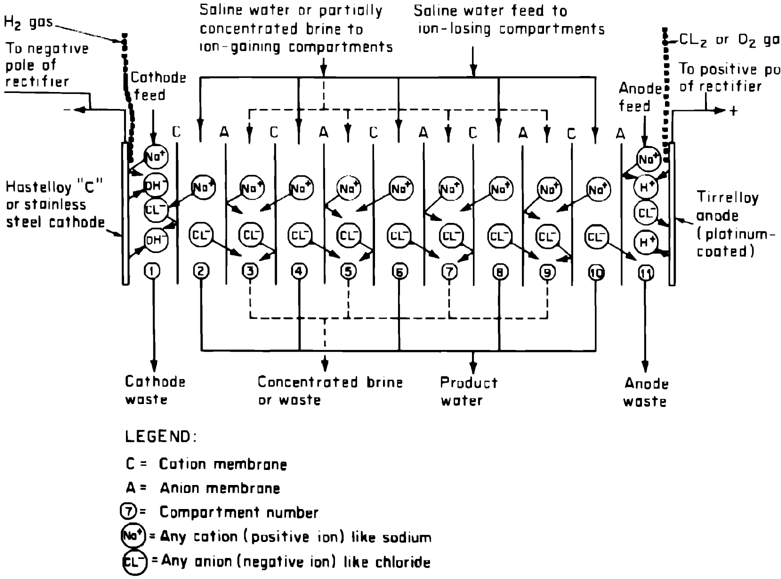
H₂ gas
To negative pole of rectifier
−
Cathode feed
Saline water or partially concentrated brine to ion-gaining compartments
Saline water feed to ion-losing compartments
CL₂ or O₂ gas
To positive pole of rectifier
+
Anode feed
C A C A C A C A C A
Na⁺
OH⁻
CL⁻
H⁺
Hastelloy "C" or stainless steel cathode
Tirrelloy anode (platinum-coated)
1 2 3 4 5 6 7 8 9 10 11
Cathode waste
Concentrated brine or waste
Product water
Anode waste
LEGEND:
C = Cation membrane
A = Anion membrane
7 = Compartment number
Na⁺ = Any cation (positive ion) like sodium
CL⁻ = Any anion (negative ion) like chloride

Fig. 10 Basic ion and water flow in an electrodialysis stack *(Ionics, Incorporated)*.

and contains manifolds for separate feed and collection of waste and product streams. Membrane stacks are manufactured having up to several hundred pairs of membranes in a single array and current designs go up to approximately 1 square meter in size. Membrane thicknesses generally vary from as little as 5 to as much as 20 or 30 thousandths of an inch.

When first developed, ED membranes had relatively short lives and were subject to scaling with deposits of calcium salts. As the membranes and the process have been improved, the life of ED membranes has now reached 5 to 10 years for the most rugged types, with the result that process costs have been correspondingly reduced.

The design of ED equipment for saline water conversion is a task for the specialist. There is a substantial amount of literature on both the theory and practice of electrodialysis, including a significant amount of data from users on operating and maintenance costs.

From the point of view of the water utility engineer, the following factors are of importance:

1. ED plants having capacities up to about a million gallons per day are in operation at a number of locations throughout the world and have proven their reliability to produce freshwater for utility use.
2. ED plants require clear waters, free from iron, manganese, turbidity, and organic matter for optimum operation. Accordingly, pretreatment of groundwaters by conventional means is sometimes required prior to ED plants and is always required prior to ED plants operating on surface water.
3. Data on the life of key components of ED plants, membranes, spacers, and electrodes are available from existing plants and are important in determining total costs.
4. ED plants will generally require from 10 to 30 per cent of the feedwater to carry off the concentrated salts and minerals removed.

Freezing

If saline water is frozen in such a way that salt crystals or brine pockets are not trapped in the ice crystals, the resulting ice will be essentially free of minerals. The mineral-free ice can be carefully separated from the brine and melted, to produce potable water from saline waters. This process and its variants have attracted much attention over the past decade or more. Freezing has two inherently interesting properties as compared with distillation processes:

1. The heat of freezing and melting is on the order of one-seventh as much as the heat of evaporation and condensation. Therefore, less heat energy must be transferred per pound of water produced. (This apparent advantage is tempered since heat transfer rates are generally slower at low temperatures and the energy required to cause freezing is the more costly work energy.)

2. Because of the low temperatures at which freezing takes place, corrosion problems can be expected to be less than those encountered at the relatively high temperatures required for distillation.

Freezing, on the other hand, requires the handling of a solid mass of crystals and their efficient separation from brine clinging to these crystals. The handling and separation of these solid crystals is the central engineering problem of freezing processes. At the present time, only a few pilot plants using freezing have been operated and these plants have not yet demonstrated the predicted cost advantages. However, substantial development work continues on freezing.[40,41,42]

Reverse Osmosis

Over the past decade very thin membranes have been synthesized from cellulose acetate and more recently from nylon. These membranes will pass relatively pure water and retain relatively salty water when a saline water is forced against them by high pressure. This filtration-like process is generally referred to as reverse osmosis or RO (Fig. 11).

Since the development of the first membrane having an acceptable combination of permeability or "flux" and salt rejection in the early 1960s,[43] the University of California, Office of Saline Water, and a number of private firms have been active in the development of various types of RO equipment. RO units of different types and sizes have been built and operated for various periods, mostly under government or private research auspices. Most units have ranged from laboratory scale to a few thousand gallons per day. Several units in the 50,000- to 100,000-gpd range have been assembled, but significant field data or field experience are not yet available on these larger units.[17,37,44]

RO has several promising inherent characteristics:

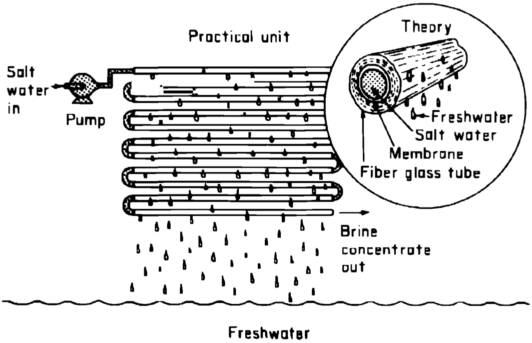

Fig. 11 Simplified illustration of tubular reverse osmosis *(U.S. Department of the Interior, Office of Saline Water).*

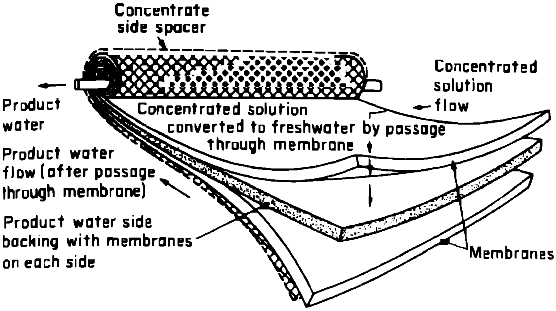
Concentrate side spacer
Concentrated solution flow
Product water
Concentrated solution converted to freshwater by passage through membrane
Product water flow (after passage through membrane)
Product water side backing with membranes on each side
Membranes

Fig. 12 Diagram of spiral-wound reverse osmosis module, partially unrolled *(U.S. Department of the Interior, Office of Saline Water).*

1. It is simple in basic concept.
2. Unlike distillation, it does not require heat transfer.
3. The first practical membrane was synthesized from cellulose acetate, a relatively cheap material.
4. It appears that with further development work, the process will be useful for brackish water treatment, for treatment of wastewaters, and ultimately for seawater.

There are a number of variants of RO equipment being developed:

1. *The flat plate,* in which flat sheets of membranes are forced against filter plate leaves somewhat in the manner of a conventional filter press.[45]
2. *Tubular,* in which the membrane is cast or affixed into the inside of a porous or perforated piece of tubing.[37,44,46] Tube diameters as little as ¼ in. to as large as 2 in. have been proposed and built.[47]
3. *Spiral or jelly roll,* in which an envelope of RO membrane is formed by sealing the edges but not the ends of a folded flat sheet. A plastic mesh separator is placed inside the envelope and another outside and the whole structure is then rolled up into a spiral and inserted into a pressure vessel. Saline water in the pressure vessel is pressurized against the "outside" of the rolled-up envelope, and pure water flows through the membrane walls of the envelope and then along the interior spiral path to the open end of the envelope[37,48] (Fig. 12).
4. *Hollow fiber.* This development represents the ultimate in the tubular concept. Hollow fibers about the size of human hairs are spun by modified textile fiber spinning machinery.[49] A bundle of fibers is collected and the ends encased in a solid plug of plastic sealing material. A cut through the plug exposes the hollow ends of the fibers and the bundle is inserted into a pressure vessel.[50] Pressurized saline water forces pure water through each fiber wall and then along the inside bore to the exposed fiber ends where it drips out and is collected as product (Fig. 13).

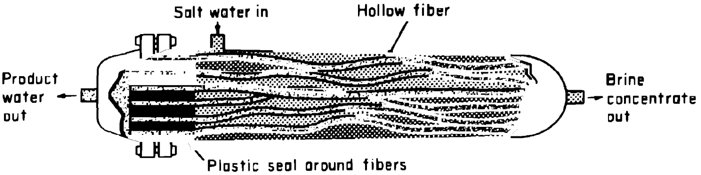

Fig. 13 Simplified illustration of hollow-fiber reverse osmosis process *(U.S. Department of the Interior, Office of Saline Water).*

Certain problems of the RO field are under intensive study and development:

1. Cellulose acetate is an inexpensive material but is sensitive to pH changes in the water, to oxidizing agents, possibly to bacterial action, and to compaction under the pressures required. Membrane life estimates have ranged from as little as a few months to as much as 3 years. The recently introduced nylon fibers have considerably greater chemical resistance than cellulose acetate, but current formulations have about a one-hundredth the permeability of cellulose acetate. It is not yet clear how costs of water produced by the nylon system will compare with that produced by cellulose acetate systems.

2. Since the RO membrane literally filters water, RO is sensitive to particulate material, iron, manganese, turbidity, organic substances, and certain other undissolved impurities in the water. Considerable attention is now being given to the pretreatment requirements for RO plants. There may be significant differences among the various RO processes in the need for pretreatment.

3. While the raw material cost of membrane surface based on cellulose acetate is very low per square foot, the problems of mounting, supporting, detecting failures, and replacing membranes result in significant additional costs both for plant and replacement.

4. The high pressures employed in RO equipment (generally 400 to 1,500 psi) require efficient and reliable pumping equipment and relatively costly piping, fittings, and pressure vessels. The development of the necessary pumping equipment to handle saline water is recognized as a major need in the RO field.[51]

Ion-exchange

Ion-exchange processes (IE) have been used for 30 or more years for the so-called "zeolite" softening of water and more recently for demineralization by the use of both cation and anion beds or mixed beds regenerated by acid and alkali. Increased interest in saline water conversion, and particularly brackish water conversion, has led to new developments in the IE field with the objective of broadening the range of TDS over which IE is useful. Up until recently, IE was not much used for demineralization on waters containing more than a few hundred ppm TDS, since both the size of the required IE beds and the amounts of chemical regenerant required became prohibitive.

Theoretically, at least one equivalent of acid and one equivalent of alkali is required in IE processes for the removal of one equivalent of salt or mineral from water. In processes available up until recently 2 to 3 equivalents of acid and 1.2 to 2.0 equivalents of alkali per equivalent of salt removed were required. Developments in IE which give promise of extending the useful range of IE demineralizers up to at least 1,000 ppm TDS and possibly to as much as 2,000 ppm include combinations of one or more of the following:

1. Newer resins which can be regenerated by weaker and less expensive acids and alkalis such as carbon dioxide, ammonia, and lime[52,53]
2. Newer resins which can be regenerated by 1.1 to 1.5 equivalents of acid or alkali per equivalent of salt removed
3. Resins of high capacity per cubic foot[54]
4. The use of continuous movement of IE resin beds[55]

As an extreme case, it is possible in one of the new IE processes to use water alone—rather than alkali—to regenerate the anion bed if the water to be demineralized is a high-sulfate water. However, relatively large volumes of water are needed for this water regeneration, so that this particular variant—while interesting—will probably not find wide usage in the water utility field. On the other hand, if the same process is utilized with relatively small amounts of lime or ammonia, the amount of water required for regeneration is reduced to acceptable levels.

Very few installations using the newer proposed IE demineralization processes have been built. The Office of Saline Water has contracted for field tests on these processes and cost data from field experience should be available before too long. IE processes have a number of potential advantages for saline water conversion.

1. For relatively low ppm waters of 500 to 1,500 ppm total dissolved solids, the capital investment may be lower than for membrane processes.
2. For waters containing large amounts of bicarbonate, the anion cycle may be omitted.

On the other hand, IE has certain inherent problems:

1. Chemicals are used to remove other chemicals and the total effluent from the plant (product plus wastewater) will contain substantially more mineral material than the feedwater, thus aggravating the already difficult problem of waste disposal for saline water conversion plants.
2. Ion-exchange is a multistep process requiring use of large amounts of acids and alkalis, precise chemical control to assure economy, and either

movement of solid resins or frequent switching of streams. IE processes thus present more problems in reliability and control than the more continuous thermal or electrical processes.

3. In the event of human or mechanical errors, the feeding of any form of alkali into the type of saline waters found in most of the United States presents a fair possibility of hard scale deposition.

4. Effective control of an IE demineralization process requires personnel with a high degree of chemical and chemical engineering knowledge. Most large IE demineralizers built to date have been constructed for use in the public utility, chemical, and process industries.

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19

Management of Water-treatment Plant Residues

By JOHN T. O'CONNOR

A residue is a remnant, a substance which remains after another part has been taken away. In water treatment practice, where suspended and dissolved constituents are separated from water in order to effect purification, a variety of residues remain after the product water is dispensed. It seems imprudent to refer to all of these residues as "wastes," since that term clearly implies that no beneficial use can be made of the residue and that it is to be discarded. The thinking of waterworks engineers should not be confined to the disposal of water-treatment plant residues in the most convenient manner and at minimum disposal cost. Instead, at least at the outset, residues from water-treatment plants should be considered as potentially useful by-products in hopes that such an attitude may result in the development of more and more imaginative techniques for utilization of residues.

The following discussion considers the sources and nature of water-treatment plant residues; some methods currently used for their disposal and for reclamation of useful by-products; and, finally, some aesthetic and legal aspects of disposing the residues to natural water courses.

SOURCES OF WATER-TREATMENT PLANT RESIDUES

In approximate order of abundance, the residues from water-treatment plants can be classified as:

Residues from Chemical Coagulation

Since aluminum and iron salts are generally used to accomplish coagulation, hydrated aluminum and iron oxides, often referred to as aluminum and ferric hydroxides, are the chief constituents of sludges from water-treatment plants practicing chemical coagulation. In addition to these hydrates, the residues contain entrained particulate matter, both organic and inorganic. In the absence of gross pollution of the raw water source, the entrained or absorbed organic fraction of the residue is small and, for the most part, stable or nonputrescible. Because of this, residues from coagulation are allowed to accumulate in settling tanks over long periods of time, varying from days to months, and then discharged intermittently. Although BOD values of these residues might be in the hundreds of mg/l and COD values might be in the thousands of mg/l,[1] the sludges are still considered stable since they do not undergo active decomposition or promote anaerobiasis.

Most of the matter entrained in coagulation is inorganic in nature and consists of fine sands, silts, and clays.

Residues from Softening by Chemical Precipitation

Softening of groundwaters by chemical precipitation with lime (CaO) and soda ash (Na_2CO_3) yields a relatively pure residue, free of extraneous inorganic and organic matter. The residue most frequently consists of calcium carbonate, magnesium hydroxide, and unreacted lime. Because of the poor settling properties of the colloidal fraction of this residue, softening is normally supplemented with coagulation. As a result, a fraction of the residue removed in the settling tank consists of hydrated iron or aluminum oxides.

There are two fractions of residues from water-softening plants, therefore: precipitates drawn from the bottom of softening reactors and coagulated precipitates drawn from the bottom of settling tanks. Of the two, there is a far greater quantity of the former.

Residues from water softening are generally stable, dense, inert, and relatively pure. It is for these reasons that recovery of lime by recalcination is a relatively attractive proposition for large plants.

Residues from Backwashing of Filters

All water-treatment works which practice filtration through coarse media produce a large volume of washwater containing a low solids concentration due to their filter washing operations. Filters are often washed on a daily basis. The volume of water used is large because the wash rate may be ten to twenty times the filtration rate. Two to three per cent of all the water filtered may be used for filter washing. The solids content of the filter washwater reflects the efficiency of the pretreatment while the composition of the solids is generally similar to that of the other solids produced. In many instances a very substantial fraction (30 to 40 per cent) of the total solids produced in a water-treatment plant appears in the backwash water. An extreme case occurs in plants practicing iron removal where 50 to 90 per cent of all solids removal may occur in the filters.[2] When activated carbon is applied directly prior to filtration, the filter backwash water will also contain the bulk of the carbon applied.

Diatomaceous earth filtration has an advantage over coarse media filtration in that there is virtually no backwash water to be disposed of.

Settled Solids from the Presedimentation of Raw Water (Siltation Basins)

Where surface waters are withdrawn from water-courses which contain a large quantity of suspended materials, presedimentation prior to coagulation may be practiced to reduce the accumulation of solids in subsequent treatment units. The settled material generally consists of fine sands, silts, clays, and organic debris of vegetable origin. Solids may be allowed to accumulate for months or years and subsequently be removed by dredging.

Residues from Iron and Manganese Removal

The volumes of water treated, specifically, for iron and manganese removal are small compared with the volumes coagulated or softened. Most often, iron and manganese are removed by precipitation processes, as hydrated ferric and manganic oxides. Since the concentrations of iron and manganese in ground and lake waters are generally low, the volume of solids produced is correspondingly small.

Spent Activated Carbon

Periodically, lake and other surface water supplies exhibit strong tastes and odors which are associated with algal blooms. These conditions may persist for a matter of weeks or throughout the entire summer. To a large extent, applications of activated carbon are used to reduce the odors. The relatively high cost of activated carbon ensures that the dosages applied for odor control will not be excessive. The contribution of activated carbon to the volume of water-treatment residues is therefore small. The determination of COD on water-treatment plant residues containing activated carbon will yield high values, perhaps on the order of 10,000 mg oxygen/l.[1]

Spent Diatomaceous Earth

Diatomaceous earth is used in a number of comparatively small water-treatment works as a filter medium.[3] After each filter cycle, the media and accumulated solids are discarded and the filter medium reestablished on the filter septum by means of a "precoat." During filtration, diatomaceous earth is added as a "body feed" to prolong the filtration cycle. Since the amount of municipal water treated in this fashion is small, the amount of solids accumulated is small. Moreover, the solids which are produced are primarily pure silica and are very easily dewatered. It is of special interest to note that many of the filtration systems for swimming pools in this nation employ diatomaceous earth.

Residues Resulting from the Use of Coagulant Aids (Polyelectrolytes, Clays, Activated Silica)

Although the potential for the use of organic polyelectrolytes for chemical coagulation is great, the cost of these materials has relegated them to limited use as coagulant aids in waterwork practice. The use of polyelectrolytes, either alone or as a coagulant aid, results in a somewhat lowered solids production.

Clays, such as bentonite, and activated silica are added to some waters to provide negatively charged particles for coagulation and to increase sludge density.

Spent Brines from Regeneration of Ion-Exchange Units

The spent brines from the regeneration of ion-exchange softeners form a special class of water-treatment residues, those which are in aqueous solution. Depending upon the raw water hardness and the operation of the exchange unit, the volume of brine residue may range from 3 to 10 per cent of the treated water.[4] The residues consist primarily of the regenerant salt, NaCl, plus the calcium and magnesium ions displaced from the exchange resin.

In summary, the residues produced by water utilities are derived primarily from chemical coagulation, lime-soda softening, filter backwashing and, to a lesser extent, from presedimentation of raw water, iron and manganese removal, disposal of diatomaceous earth, use of activated carbon and coagulant aids, and regeneration of ion-exchange units. On the whole, these wastes are stable or nonputrescible and are therefore collected or discharged intermittently rather than continuously.

CHARACTERISTICS OF RESIDUES FROM WATER-TREATMENT PLANTS

Chemical Analysis of Water-treatment Plant Residues

Residues from Coagulation with Aluminum Salts. Chemical analyses of residues produced by coagulation with aluminum salts have yielded little significant information about the solids themselves, although this may be estimated from a knowledge of the coagulant employed. Normally, the pH of the slurry is near neutral, in the range of 6 to 8. The 5-day BOD of a slurry has been measured, but is probably not as significant as the long-term BOD. Table 19-1 shows the oxygen demand determined at 5, 7, and 27 days for aluminum coagulation residues from a 25-mgd water-treatment plant (plant A). The continuing increase may be taken as an indication of the low rate of biodegradability (exertion of oxygen demand) of the organic matter present.

The high ratio of COD to BOD_5, 13:1, is a further indication of the stability of the organic fraction.

For plant A, the total suspended solids concentration yields a 0.1 per cent solids concentration. This is on the low side, since residues from aluminum coagulation are often in the 0.5 to 2 per cent solids concentration range. The volatile fraction of the suspended solids is about 56 per cent of the total suspended solids. This does not reflect the fraction of organic matter present, however, as much of the loss on ignition was probably water bound by the hydrated aluminum oxide. Overall, the analysis commonly run on these sludges does not serve to clearly determine its chemical composition.

Residues from Coagulation with Iron Salts. The solids produced from the coagulation of water by iron salts are similar to those produced by coagulation with aluminum salts. The obvious difference is that the bulk of the residue consists of hydrous ferric, rather than aluminum, oxides. Since ferric oxides are insoluble over a far wider pH range than aluminum oxides, the pH of the water in contact with hydrated iron oxides may be found to vary over a wider range. Partly for this reason, iron salts are widely used for coagulation following softening and for the removal of color from soft waters. Chiefly because of cost, aluminum coagulants are more widely used in water-treatment practice than iron. In 1965, the annual consumption of alum was 600,000 tons as opposed to 100,000 tons per year for iron salts.[5]

TABLE 19-1 Characteristics of Aluminum Coagulation Sludge (after Russellmann[1])

Plant	BOD, mg/l	COD, mg/l	pH	Total solids, mg/l	Volatile solids, mg/l	Total suspended solids, mg/l	Volatile suspended solids, mg/l
A	41(5-day) 72(7-day) 144(27-day)	540	7.1	1,159	571	1,110(0.1%)	620
B	90(5-day)	2,100	7.1	10,016	3,656	5,105(0.5%)	2,285
C*	108(5-day)	15,500	6.0	16,830	10,166	19,044(1.9%)	10,722
D	44(5-day)	......	6.0	......	......	15,790(1.6%)	4,130

*This sample contained activated carbon.

Residues from Softening by Chemical Precipitation. The composition of sludges from the precipitation of hardness by lime and soda varies with the composition of the raw water and the dosages of chemicals used for softening. Table 19-2 shows the results of the chemical analysis of dry solids from three water-softening plants.[6]

TABLE 19–2 Chemical Composition of Dry Solids from Water Softening

Constituent	Per cent by weight		
	Boulder City, Nev.	*Miami, Fla.*	*Cincinnati, Ohio*[*]
Silica, iron, and aluminum oxides	2.6	1.5	4.4
Calcium oxide, CaO	48.8	52.1	49.3
Magnesium oxide, MgO	7.0	2.8	2.2
Loss on ignition or CO_2	38.4	43.8	40.2
Equivalent $CaCO_3$	87.2	93.0	88.1

[*] Wright Aeronautical Corporation.

It is evident that for these waters, each initially low in magnesium, the precipitates are about 90 per cent calcium carbonate plus 2 to 7 per cent magnesium oxide. These results are not entirely typical, since many water-softening plants produce residues with a much higher proportion of magnesium oxide.

Backwash Waters. Solids in filter backwash waters, as noted previously, resemble the settled materials found in pretreatment, usually sedimentation, units. Hydrous oxides of aluminum, iron, manganese, and magnesium; carbonates of calcium and iron; plus silicate materials form the largest fraction of the solids. Organic matter may be present in the form of algae, plankton, slime-forming bacteria, and spent activated carbon. Since rapid-sand filters can often support a luxurious biological growth, the filter backwash may contain a far larger fraction of organic matter than is found in the solids from sedimentation units. Moreover, the bacterial count of filter backwash waters can be quite high.

Table 19-3 provides some data on the characteristics of various filter backwash waters. Very low values for BOD_5 and relatively high values for COD are an indication of the presence of a small amount of relatively stable organic matter. In those plants where aluminum coagulation is practiced, both total solids and suspended solids are very low. The average for suspended solids in the filter backwash water is less than 0.01 per cent.

The backwash water from the filtration plant removing iron and manganese, however, is far higher in suspended matter (0.14 per cent). Subsequent settling will, in some instances, yield higher solids concentrations, possibly approaching those concentrations achieved in the settling tanks prior to filtration. However, more often, chemical coagulation or physical

TABLE 19-3 Characteristics of Filter Backwash Water (after Russellmann[1])

Plant treatment	BOD_5, mg/l	COD, mg/l	pH	Solids, mg/l			
				Total	Volatile	Suspended	
						Total	Volatile
A. Aluminum coagulation	4.2	28	7.8	121	44	47	31
B. Aluminum coagulation	3.7	75	7.2	378	115	104	53
C. Aluminum coagulation	2.8	160	7.8	166	45	75	40
D. Aluminum coagulation	1.8	....	...	.....	...	100	60
E. Iron and manganese removal	...	....	6.9	1,487	343	1,370	400

removal processes are required for concentration of the solids in backwash waters.

Chemical analyses of backwash waters from two of Detroit's four municipal water-treatment plants which employ aluminum sulfate as a coagulant for Detroit River water are given in Table 19-4. These analyses reveal that aluminum and silicon oxides predominate, while carbon and organic matter comprise roughly one-fifth of the residue. Coliform counts are minimum, but the total bacterial count is not wholly insignificant. The low chlorine demand attests to the stability of the organic fraction of the residue.

TABLE 19-4 Analyses of Backwash Water from Detroit Plants (after Remus[7])

Substance	*Amount*
Water Works Park plant (318 mgd)	
Al_2O_3	25%
SiO_2	36%
Carbon and organics	22%
Turbidity	600 j. u. (800 mg/l residue)
Coliform group	0.0 MPN
Bacterial plate count	230/ml
Springwell's plant (480 mgd)	
Al_2O_3	50%
SiO_2	35%
Carbon and organics	15%
Chlorine demand	0.0–0.18 mg/l in 1 hr
Coliform group	0.0 MPN

Spent Brine Solutions. The analysis of a particular spent brine solution is given in Table 19-5. Approximately one-half of the solid residue is sodium chloride while the remainder is almost entirely calcium and magnesium chloride.

TABLE 19-5 Analysis of Spent Brine Solution (after Haney[4])

Constituent	mg/l	meq/l
Sodium and potassium	3,325	145
Calcium	1,720	86
Magnesium	600	50
Chloride	9,600	270
Sulfate	328	7
Dissolved solids	15,656	

Physical Characteristics of Water-treatment Plant Residues

Some very rough estimates of some of the physical properties of residues from water-treatment plants can be obtained from the literature. A compilation of some of the data available, freely interpreted, appears in Table 19-6.

TABLE 19-6 Characteristics of Wastewaters from Various Water-treatment Processes[1,5,8,9]

Characteristic	Aluminum coagulation	Lime-soda softening	Filter backwash
% solids	0.2–2.0	2–15	0.01–0.1
Color	Grey-brown	White	Varies widely; grey—brown—black
Odor	None	None—musty	None
BOD_5, mg/l	30–300	Very low	10
COD, mg/l	30–5,000	Low	100
Bacterial count	High	Low	High
Settleability	Poor: 50% in 8 hr.	50% in a week	80% in 2 to 24 hr
Filterability, specific resistance, sec^2/g ...	Poor: 2×10^9	Poor	Poor
Viscosity, g/cm-sec ...	0.03 Non-Newtonian	....	0.01 (water)
Dewaterability	Conc. to 10% solids in 2 days on sand beds	Slowly compacts to 50% moisture in lagoons	Must be coagulated and settled

PRESENT METHODS OF DISPOSAL OF WATER-TREATMENT RESIDUES

Disposal of Solids from Chemical Coagulation

A questionnaire sent in 1952 to sanitary engineers throughout the United States yielded the following data on the disposal of residues from 1,530 water-treatment plants excluding those plants which practice primarily water softening (Table 19-7).

It is apparent that the discharge of water-treatment plant residues to

TABLE 19-7 Methods of Disposal of Residues from Water-treatment Plants (after Dean[10])

Method of disposal	*Per cent*
To streams or lakes	92.4
To storm sewers or surface drains	3.5
To sanitary sewers	0.3
To sludge beds	3.1
To city reservoirs, irrigation ditches, dry creeks, impounding basins	0.8

surface waters was nearly universal (96 per cent) practice at the time of the survey. This is still believed to be the predominant practice. However, this practice appears destined to undergo a very radical and rapid change in the near future.

Other data of interest obtained from the questionnaire pertain to the arrangement of filter plants and methods of removing residues from settling basins.[10] Three-quarters of the filter plants surveyed employ coagulation and sedimentation prior to rapid-sand filtration; 17 per cent employ filtration alone, generally by slow-sand filters; 6 per cent employ presedimentation prior to coagulation and sedimentation. As for solids removal from settling tanks, 91 per cent of the plants employ flushing and fire streams for intermittent solids removal; the other 9 per cent of the settling basins have mechanisms for continuous solids removal.

It is evident from the results of the questionnaire that, with one notable exception, virtually no plant studies had been made of solids concentration by vacuum filtration. In addition, the respondents to the questionnaire indicated that there was no demand for the waste solids as a fertilizer.

In summary, the disposal of the settled solids from chemical coagulation is nearly universal and straightforward—intermittent discharge to the nearest body of natural water.

Disposal of Filter Backwash Water

Filter washings are disposed of in approximately the same fashion as residues from chemical coagulation. The survey of disposal techniques at 1,699 water-treatment plants reveals the following (Table 19-8):

TABLE 19-8 Disposals of Filter Washings (after Dean[10])

Method of disposal	*Per cent*
To stream or lake	82.6
To storm sewer or surface drain	10.7
To sanitary sewer	2.5
To lagoons from which solids are not removed	1.9
To dry creeks	0.8

Since filter washings have turbidities less than 500 j. u., it is generally felt that it was not objectionable to discharge them into streams or lakes. Moreover, 516 out of 1,601 water-filtration plants chlorinate prior to filtration. This practice was deemed beneficial in controlling growths of bacteria in filter washings.[10]

Disposal of Chemical Precipitates from Softening

The results of a survey of the state sanitary engineers from the 21 states in the United States having the largest number of water softening plants were reported in 1949.[11] Data were obtained for 371 lime or lime-soda softening plants, the majority of which were in Ohio (109), Illinois (41), Florida (31), Kansas (26), Pennsylvania (23), Iowa (20), and Missouri (19). The methods of solids disposal at these plants are summarized in Table 19-9.

TABLE 19-9 Methods of Disposal of Solids from Water-softening Plants (after Black and Haney, 1949[11])

Method of disposal	*Per cent*
Discharged to flowing watercourse	58.4
Disposal to sludge beds or lagoons	29.6
Discharged to storm or sanitary sewers	8.6
Discharged to watercourses other than flowing ones	2.1

The softening residues discharged to sanitary sewers at Lebanon, Indiana, were accused of causing digester upset and "plugging" of digesters. However, at Lebanon they reported that a relatively stable sludge could be obtained by mixing and lagooning primary sewage sludge with the residue from softening. In another case, the precipitates from softening, after lagooning and drying, were used for trench backfill to aid in the control of corrosion of water mains. In still another instance, the liquid slurry was disposed of by direct spreading on farm lands. This practice may hold great promise in agricultural lands where soils are acid.

Williamson[12] reports on the use of lime softening residues as a coagulant for raw sewage sludge. Pilot studies at Daytona Beach, Florida, had indicated that a BOD reduction of 70 to 80 per cent could be obtained with one hour's detention following the addition of lime softening residue to the raw sewage.

Lagooning of lime softening residues may be an interim or permanent solution to the disposal problem. As filling proceeds, the solids consolidate to approximately 40 to 50 per cent by weight as the supernatant is withdrawn. The filled lagoon, in some cases, may be covered with topsoil and grass. Assuming 50 per cent moisture, the lagoon capacity for lime softening residues averages about 0.6 acre-foot/ year (mgd) (100 ppm hardness removed).[13]

A most important method of disposal of softening residues high in calcium carbonate is by recalcination for recovery of lime. A separate discussion of this method is given in a following section.

Disposal of Spent Brines

Brines have been discharged to streams, lakes, sanitary sewers or into groundwaters through lagoons or disposal wells. In some cases, they have been stored in lagoons for intermittent discharge when dilution water was available. Evaporation of brines, which is slow owing to lowered vapor pressures at high salt concentrations, results in the accumulation of a salt cake which also presents a disposal problem. Deep injection wells, 400 to 5,000 ft, have been used primarily for the disposal of oil field brines. The danger of contamination of freshwater aquifers is great.[4]

Overall, the disposal of brines may lead to severe and persistent pollution problems, particularly where groundwaters are involved. However, the possibility of reusing the brine exists if an economical means could be found for precipitating the calcium and magnesium. Unfortunately, the ion-exchange process best lends itself to small installations, extending down to individual supplies, so that complicated methods of recovery are precluded. The irregular discharge of spent brines from innumerable small sources causes a particularly insidious pollution problem. It would appear that only discharge to the ocean is an acceptable solution to brine disposal.

PROCESSES FOR RECLAMATION OF RESIDUES FROM WATER TREATMENT

Recalcination of Lime Softening Residues

Quicklime, CaO, can be produced from lime softening residues by recalcination following dewatering and drying. The reactions during recalcination can be written as follows:

$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$$

$$Mg(OH)_2 \rightarrow MgO_{(s)} + H_2O_{(g)}$$

Since lime softening effects a net production in solids, the process of lime reclamation can be operated so as to produce more quicklime than is required for softening. The buildup of magnesium in the reclaimed lime can be troublesome. This can either be avoided by making alterations in the softening process or the magnesium oxide can be physically separated during solids dewatering by centrifugation.[14]

The water-softening plants at Dayton, Ohio; San Diego, California;

Lansing, Michigan; and Gainesville and Miami, Florida, practice recalcination. Plans are being made for the recovery of both lime and carbon dioxide at St. Paul, Minnesota.[15] Some of the features of some of the existing recalcining plants are summarized in Tables 19-10 and 19-11.

TABLE 19–10 Features of Some Recalcining Plants [6,14,16]

City	Capacity, tons/day	Cost/ton, $	Treatment
Miami, Florida	80	8.50	Thickening to 20–30% solids Centrifuging to 65% solids Horizontal rotary kilns, 2200 °F
Lansing, Michigan ...	30	16.70	Recarbonation with waste CO_2 Thickening to 20–25% solids Centrifuging to 62–67% solids Conditioning with soda ash and previously dried sludge Vertical kiln, 8.5 million Btu/ton
Dayton, Ohio	150	12.00	Recarbonation of lime residue to dissolve magnesium Thickening to 21% solids Centrifuging to 62% solids Horizontal rotary kilns, 2000 °F

The statistics given in the table indicate that, for large installations, lime recalcination can result in economies as well as reductions in the volume of solids to be disposed of. At a cost of from $16 to $20 per ton for new lime, the break-even size for recalcining plants is thought to be about 20 tons/day.[16] However, considering the cost of land for lagooning softening residues or the value of reducing the pollution of watercourses, installations of smaller size may deserve serious consideration.

Lime recalcining plants generally consist of the following components[17]:

1. Recarbonation using stack gases, 15 to 27 per cent CO_2, to redissolve magnesium oxide
2. Sludge thickeners and blenders which may increase the solids concentration to 20 to 30 per cent by weight
3. Centrifuges or vacuum filters for dewatering to 45 to 65 per cent dry solids by weight
4. Flash driers and cyclone separators using hot off-gases from the recalciner
5. Rotary kiln or fluidized bed recalciners in which $CaCO_3$ is converted to CaO at temperatures in the range of 870° to 1100°C (1600° to 2000°F)

The fluidized bed reactors have a number of advantages over the rotary

Table 19-11 Recalcining Plants (after AWWA Research Foundation[17])

Location	Approximate construction date	Rated capacity product output, tons/day	Type of dewatering equipment[1]	Type of recalciner[2]	Heat requirement, mil Btu/ton output	CO_2 recovered	Lime plant cost, $	Water plant rated capacity, mgd	Lime fed, lb/mg	Sludge/lime ratio
Marshalltown, Iowa	....	4.2	C	FC	9.66	...	....	3.5		
Pontiac, Michigan	....	....	C	FC	...	...	241,000	10	2,200	2.50
Miami, Florida	1948	80	C	RK	8.5	Yes	856,000	180	1,800	2.20
Lansing, Michigan	1954	30	C	FB	8.0	...	....	20	2,200	2.27
Salina, Kansas	1957	....	C	FC						
Dayton, Ohio	1960	150	C	RK	9.0	Yes	1,500,000	96	2,140	2.47
San Diego, California	1961	25	C	RK	9.0	...	534,000			
S. D. Warren Company[3] ...	1963	70	VF	FB	7.2					
Merida, Yucatan	1965	40	C	RK	...	Yes	....	24		
Ann Arbor, Michigan	1968	24	C	FB						
Lake Tahoe, Nevada[4]	1968	10.8	C	MH	7.0	Yes	....	7.5		
St. Paul, Minnesota[5] ..	1969	50	C	FB	6.2	Yes	1,750,000	120[6]	990	2.40

[1] C = centrifuge; VF = vacuum filter.

[2] RK = rotary kiln; FB = fluidized bed; FC = flash calcination; MH = multiple hearth.

[3] Paper mill owned by Scott Paper Company.

[4] Activated sludge disposal plant.

[5] Now under construction.

[6] Lime recalcining plant designed to accommodate future water-treatment plant capacity of 170 mgd.

kilns.[17] They can be started up and shut down more rapidly. They are more economical in operation and produce less dust. They are smaller and require less space. They produce a harder product which is not as readily slaked in air. In operation, sodium carbonate is added to the sludge prior to flash drying. During calcining in the fluidized bed, the sodium carbonate fuses and becomes a nucleus for the deposition of calcium oxide particles. In this manner, a "pellet" forms and grows until it can no longer be suspended by the gases in the calciner.

One interesting departure from the reclamation of quicklime from lime softening residue is the reclamation of calcium carbonate. Sheen and Lammers[18] found it more economical to recover calcium carbonate from the Wright Aeronautical softening plant residue. The calcium carbonate could be sold locally for $5 to $8 per ton for soil sweetening and as a filler in the manufacture of roofing materials, plastics, rubber, paint, and millboard. Reclamation of calcium carbonate or calcium oxide from lime softening residues is profitable only for larger installations. Since the majority of lime softening plants are small installations, lime reclamation, while worth serious consideration, will not likely be the solution to the problem of sludge disposal at most plants.

Increased attention must be given to minimizing the volume and moisture content of solid residues formed in precipitation processes. Softening processes in which dense deposits of calcium carbonate are formed on solid nuclei, such as sand, may have very great potential for future application.

Reclamation of Iron and Aluminum

Iron or aluminum sulfate can be reclaimed from hydrated iron or aluminum oxide residues by treatment with sulfuric acid. The reactions may be written as follows:

$$2Fe(OH)_3 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 6H_2O \tag{1}$$

$$2Al(OH)_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 6H_2O \tag{2}$$

Recovery of alum residues is practiced at the Tampa, Florida, water-treatment plant.[19] Conditions are particularly favorable for alum recovery at this plant because large dosages of aluminum (50 to 100 mg alum/l) are used for color removal. Because the concentration of solids drawn from the sedimentation tank ranges from 0.05 to 0.2 per cent, one major problem in the process is the concentration of solids. At Tampa, attempts at thickening resulted in a 1.0 per cent solids concentration. The concentrate, when treated with sulfuric acid, yielded the equivalent of a 2.5 per cent solution of commercial alum.

With the cost of sulfuric acid at $19.48 per ton and of commercial alum at

$38.08 per ton, savings of $11.74 per million gallons of water treated with reclaimed alum were anticipated as a result of pilot studies.

Recovery of the adsorbed, colored organic materials along with the alum, plus the need for intermittent lime softening, ultimately resulted in the abandonment of the alum recovery process.

Recirculation and Reuse of Filter Washwaters

The practice of recirculation and reuse of filter washwater has been found to be economical and feasible at Detroit's largest municipal water-treatment plant.[7]

The Detroit Springwell's water-treatment plant has a capacity near one-half billion gallons of water per day. It is operated so that all of its washwater, approximately 2 per cent of its total flow, is drawn into a 0.5 million-gallon reservoir and then recirculated into the rapid mixing basins for reuse. The accumulated solids, removed from the settling basins twice annually, are discharged to the municipal sewers.

During a 3-month period of low turbidities, the practice of recirculation resulted in filter runs averaging 36 per cent longer in the plant when backwash water was recycled. Final turbidities and chlorine demand were unaffected. During periods of high turbidities, there were no differences in the results, with or without recycling.

The important advantage of recycling was the saving of approximately $40,000 annual sewer charges plus an estimated $7,000 in pumping costs due to longer filter runs. Disadvantages of recycling included the buildup of plankton in the settling basin; the increased accumulation of solids in the settling basin; and the required coordination of filter backwashing and recycling.

During winter months, recirculation of washwater is also practiced at Detroit's 160-mgd Southwest Station plant. This is done because freezing interferes with the operation of the clarifiers normally used for the treatment of the backwash waters. No interference with treatment is reported as a result of this practice.

Direct recycling of backwash water is not always completely successful. Hartung[17] has stated that the return of washwater often places a load on the plant out of proportion to the value of the water saved, unless the water is treated before it is returned. He attributes the need for coagulation and settling of the backwash water prior to recycle to the manner in which the backwash water is handled. The coagulated material in the backwash water is broken up by turbulent flow in washwater troughs and sewers. In one plant owned by the Northern Illinois Water Corporation, this turbulence is avoided since filter units are submerged within the settling basins. The backwash water flows directly into the settling basin during backwash and is later refiltered. In this case, it is softened water which is reclaimed.

The quantities of alum residues produced may be reduced by economizing in the use of alum during periods when raw water turbidities are low. In many instances, the average raw water turbidity for a water supply is in the range of 3 to 10 j. u. Direct filtration may be possible for certain periods of the year.

QUANTITIES OF WATER TREATMENT RESIDUES

Hudson has estimated that residues from water-treatment plants total about 10^6 tons/year, whereas sewage-treatment plant sludges amount to about 10^7 tons/year.[20] While estimates of the total are of interest, a means for estimating current and future sludge production in a prescribed region are required for planning regional solids disposal.

One means of estimating the quantity of dry solids produced in water-treatment plants would be to estimate the quantity of solids produced per million gallons of water treated and multiply this value by the volume treated. Where water is treated for the removal of turbidity by aluminum sulfate, for example, the average turbidity and the average alum dose might be used to estimate the dry weight of solids produced per million gallons of raw water treated. It is interesting to note in this respect that while the turbidity of individual surface waters may vary greatly with time or season, the coagulant dosages applied are relatively constant. To make some rough calculations, let us assume that an average dosage of 17 mg/l (1.0 grain per gal.) of aluminum sulfate, $Al_2(SO_4)_3$, is used in coagulation practice. This dosage would correspond to about 30 mg/l (1.8 grain per gallon) of filter alum, $Al(SO_4)_3 \cdot 14H_2O$.

$$17 \text{ mg/l} \times \frac{\text{mol. wt. } Al_2O_3}{\text{mol. wt. } Al_2\,(SO_4)_3} = 17 \times \frac{102}{342} = 5 \text{ mg/l } Al_2O_3$$

If it can be further assumed that the turbidity, measured optically, can be taken as an estimate of suspended solids in mg/l, and that this turbidity is 100 per cent removed, then an order of magnitude estimate of dry solids production per million gallons of water treated can be arrived at as shown in Table 19-12.

In considering solids or residue production, it should be kept in mind that about one-half of the total amount of water delivered to municipalities in the United States is unfiltered. Therefore, no solids are recovered. Moreover, since most large United States cities use surface water (over 80 per cent of the water used), the solids produced from the treatment of groundwaters by softening and iron removal might be omitted from considera-

TABLE 19-12 Average Turbidities and Estimated Solids Production of Selected United States Water Supplies Employing Coagulation

Location	Average raw water turbidity[21]	Precipitated coagulant, mg/l	Estimated solids production, lb/million gal*
Baltimore, Maryland (Liberty Reservoir)	3	5(Al)	67
Patterson, New Jersey (Wanaque Reservoir)	10	5(Al)	128
Albany, New York (Alcove Reservoir)	5	5(Al)	84
Erie, Pennsylvania (Lake Erie)	9	5(Al)	118
Buffalo, New York (Lake Erie)	12	5(Al)	143
Akron, Ohio (Reservoirs)	5	5(Al)	84
Washington, D.C. (Potomac River)	49	5(Al)	455
Philadelphia, Pennsylvania			
Torresdale (Delaware River)	126	5(Al)	1,100
Belmont (Schuykill River)	32	5(Al)	310
Cincinnati, Ohio (Ohio River)	70	7(Fe)	650
Columbus, Ohio (Reservoirs)			
Dublin Road	40 + 170†	5(Al)	1,800
Morse Road	13 + 50†	5(Al)	570

*Turbidity assumed as mg/l of suspended solids and aluminum oxide (Al_2O_3) estimated as 5 mg/l or ferric oxide (Fe_2O_3) estimated at 7 mg/l.

†Includes 170 mg/l of precipitated calcium carbonate at Dublin Road and 50 mg/l at Morse Road.

tion. This is further justified because lime softening residues, while very abundant, may be processed to recover calcium carbonate or calcium oxide. Alternately, softening residues may be disposed of by spreading on nearby farmlands where soils are acid in character.

It may be that special consideration need not be given to the solids from backwash waters since it is likely that future waterworks practice may make it desirable to recycle backwash waters. Such a practice would validate the assumption that 100 per cent of the suspended matter in the raw water would be recovered.

In summary, then, the primary source of water-treatment plant residues are those large municipal plants treating surface water by coagulation and sedimentation, serving perhaps 60 million people with 10 bgd. If the average solids production, as estimated from Table 19-12, is around 300 lb per million gallons treated, the total solids production would be about 3×10^6 lb/day, 10^9 lb/year, or 0.5×10^6 tons/year.

The estimates made from Tables 19-11 and 19-12, if trustworthy, indicate that softening results in the largest solids production per million gallons of water treated, about 5,000 lb per million gallons. Water supplies drawn from rivers result in the next highest solids production, about 600 lb per million gallons. Finally, waters drawn from lakes and reservoirs result in lowest solids production, about 100 lb per million gallons. These figures may be sufficiently accurate for first approximation estimates of quantities of water-treatment plant residues to be found in specific regions for planning purposes.

DISPOSAL OF WATER-TREATMENT PLANT RESIDUES: ENVIRONMENTAL CONSIDERATIONS

The discharge of residues from water-treatment plants to natural watercourses has led to problems which have become severe in many instances. The most obvious effect of the discharge of these solids to a stream is the buildup of deposits or "sludge banks" in the backwaters of slowly moving portions of the stream. In turn, these deposits may cover over and thereby retard the growth of benthic organisms which serve as a source of food for fish life. Spawning and breeding of fish may also be impaired by such deposits.

From an aesthetic standpoint, the discharge of water-treatment residues is objectionable because it will markedly increase the turbidity and apparent color of the receiving waters. This may seriously decrease the recreational value of such waters. Increased turbidity may promote other, more subtle, biological and chemical changes in receiving waters. Decreased light penetration will result in decreased photosynthetic activity among aquatic plants. Suspended particles may provide surfaces for bacterial growth. The oxygen demand of these residues, while small and exerted at a low rate, is certainly of no benefit to a stream. All of these problems are aggravated when disposal of these residues is to lakes rather than streams, or, more insidiously, to streams which are tributaries to downstream impoundments.

The possibility of bacterial contamination of receiving waters by the discharge of filter washwaters is probably far greater than most people realize. Rarely are microbiological analyses made of filter washwater since it is assumed that pretreatment, including prechlorination, improves the bacterial quality of backwash water over that of the raw water.[7] On the other hand, luxurious growths of microorganisms are commonly found in filters even where the water undergoes prechlorination, and as a result, bacterial plate counts of backwash waters may be quite high. Even residues from settling tanks have been found to have bacterial counts in excess of 1,000 per milligram of solids.[10]

The increasing use of activated carbon for the control of tastes and odors has attracted attention to the discharge of filter washwaters owing to the intense, dark color imparted by the carbon.[1] In some instances, particularly where bathing beaches are involved, the removal of spent carbon prior to washwater discharge is indicated.

LEGAL ASPECTS OF THE DISCHARGE OF WATER-TREATMENT PLANT RESIDUES

State Quality Standards

Do water-treatment plants have a right to discharge residues to watercourses? Is this practice justified by the fact that the solids being returned to a watercourse originated in that watercourse? According to the Attorney General of Pennsylvania as far back as 1938, it does not.[7] It was ruled that it is the discharge that is important, and not the source from which the industrial wastes arise.

Pennsylvania regulations restrict discharges from mineral preparations plants to a concentration of 200 ppm. Since the solids in filter washwaters may range from 10 to 1,000 ppm, either dilution or removal of solids may be indicated. Pennsylvania also attempts to prevent the discharge of carbon to receiving streams by requiring treatment for removal of carbon.[7] These regulations have been strictly applied to all new water-treatment plants since 1959 under Pennsylvania's somewhat unique and far-seeing Clean Streams Act.

Federal Pollution Control Regulations

The Water Quality Act of 1965, which established the Federal Water Pollution Control Administration (FWPCA)—recently renamed the Federal Water Quality Administration (FWQA)—gives the Administration enforcement powers to control pollution of interstate waters. Standards of stream water quality, established by the individual states and approved by the FWQA, set limits on the wastes discharged to a given watercourse. Since the federal legislation does not distinguish between the sources of pollution, water-treatment plant discharges which lead to degradation of stream quality below the established levels fall subject to the law. It is now necessary, therefore, to consider the effect of the discharge of water-treatment plant residues on the quality levels set for the receiving waters.

Survey of Regulatory Agencies

In 1968, the AWWA Research Foundation[17] conducted a survey by sending questionnaires to regulatory agencies regarding the disposal of wastes from water-treatment plants. There were 59 respondents, including all the states (except Nevada), the District of Columbia, Guam, Puerto Rico, the Virgin Islands, and six interstate agencies. A brief summary of the results of this survey is presented in Table 19-13.

The response to the first five questions clearly indicates that these agencies are active in controlling pollution problems caused by the discharge of water-treatment plant wastes to surface waters. However, the response to the last five questions indicates that the agencies are operating

TABLE 19-13 Results of AWWA Research Foundation Survey (1968)[17]

Question	*Yes*	*No*
1. This agency considers discharge of these wastes to surface waters a violation of pollution control laws or regulations.	49	4
2. This agency has laws or regulations requiring control or treatment of these wastes before discharge to surface waters.	45	5
3. This agency plans future laws or regulations for control or treatment of these wastes before discharge to surface waters.	11	36
4. This agency has encountered pollution problems attributed to the discharge of these wastes to surface waters.	30	19
5. This agency has taken official or unofficial action to discontinue the discharge of these wastes to surface waters.	34	19
6. This agency has available reports and data on the quantities and characteristics of these wastes.	6	49
7. This agency can identify water-treatment plants having facilities for control or treatment of these wastes.	33	23
8. This agency can identify water-treatment plants discharging these wastes to sewage systems.	20	33
9. This agency has previously conducted or supported research on the treatment of these wastes.	1	52
10. This agency is currently conducting or supporting research on the treatment of these wastes.	2	51

under an appalling burden. It appears that many of them have little information on the sources, characteristics, current disposal practices and treatment of water-treatment plant wastes. Moreover, the survey indicates that virtually no research is being done with the support of these agencies.

Research

While there may be a question as to which agencies (federal, state, municipal or private) should support research on methods for the management of water-treatment plant residues, there is little question that research in this area is desperately needed. Some of the research conducted to date is summarized in Table 19-14. It is evident that little or no basic research is being done on the physical (rheological) properties of the suspensions produced in water-treatment plants. Little data is available on viscosity, settling properties, thickening characteristics, filterability, surface properties, and the chemical composition of the various residues. The lack of emphasis on this type of research has and will continue to inhibit progress in this area. Since there are few techniques by which the characteristics of suspensions may be defined, the results of empirical studies on ill-defined suspensions are often contradictory and cannot be correlated.

Perhaps the most interesting, important, and comprehensive study of the ultimate disposal of solid residues has been conducted by the Bechtel Corporation under sponsorship of the Federal Water Quality Administra-

TABLE 19–14 Research on Management of Water-treatment Plant Wastes (after AWWA Research Foundation [17])

1. Methods for solids concentration and dewatering
   - *a.* Freezing and thawing of alum residues
   - *b.* Heat treatment of alum residues
   - *c.* Acidification to improve thickening
   - *d.* Polyelectrolyte and lime treatment to improve filterability
   - *e.* Improvements in thickener design
   - *f.* Vacuum filtration of alum residues
   - *g.* Centrifugation of alum residues
   - *h.* Drying of alum residues on sand beds
   - *i.* Lagooning of lime softening residues
   - *j.* Use of the filter press for dewatering alum residues
2. Methods for reclamation
   - *a.* Recovery of aluminum sulfate using sulfuric acid
   - *b.* Recalcination of lime softening residues
   - *c* Utilization of alum residues in industrial processes as wetting agent, binder, or filler
   - *d.* Utilization of residues for land reclamation and agriculture
3. Ultimate disposal

   Pipeline transport of residues to land reclamation or disposal areas

tion.[22] This study, completed late in 1969, considered the economic and engineering feasibility of transporting slurries by pipeline to strip-mine disposal areas for land reclamation. Residues from a variety of sources, including those from dredging operations as well as from water- and waste-treatment plants, might be collected over a broad region and transported to a disposal region. The economies of scale for treatment, reclamation, and management inherent in such a system may be very great. The Bechtel research included a field study of pipelining waste-treatment plant sludge using a test facility at Cadiz, Ohio, to determine the hydraulic characteristics of slurries with high solids content. The study also considered various aspects of ocean disposal for coastal regions.

This approach to the management of wastes and residues, although bounded by many political constraints, may ultimately prove to be the most realistic one, particularly in regions of high population density.

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